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ANALYSIS OF FOOD AND DRUGS, AND OF GENERAL  
ANALYTICAL AND MICROSCOPICAL RESEARCH.

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# THE ANALYST.

JANUARY, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

AN ordinary meeting of the Society was held at Burlington House, on Wednesday, the 12th December, the President, Mr. Allen, in the chair.

The minutes of the November meeting were read and confirmed.

Mr. Turner was appointed to act with Mr. Fox in auditing the accounts for the past year.

The following gentlemen were proposed for election :—As members, Mr. T. S. Gladding, New York ; Professor V. Stein, Government Laboratory, Copenhagen. As associate, Mr. Sydney Steel, assistant to Mr. Bernard Dyer.

On the ballot papers being opened, the following gentlemen were declared duly elected :—As member, Mr. R. W. Woosnam, London, analyst to the Dairy Supply Company. As associate, Mr. A. J. Starey, assistant to Mr. L. Briant.

The following papers were read and discussed :—

“On the Determination of Citric Acid in Lemon-juice.” By Rowland Williams.

“On some Abnormal Samples of Butter.” By the President.

A long discussion ensued, and ultimately a Committee was appointed, as reported on page 17.

“The Werner-Schmidt Method of Determining Fat in Milk and Cream.” By A W. Stokes.

“On the Examination of Lard for Adulteration.” By T. S. Gladding.

“On the Action of Iron Pipes on Water Conveyed Therein.” By S. Harvey.

The annual meeting of the Society will be held on the 9th inst., at Burlington House, and afterwards the annual dinner will take place. Full particulars will be duly announced.

## DETERMINATION OF THE MELTING POINTS OF SOAP-THICKENED OILS.

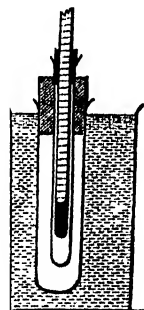
By W. F. K. Stock, F.C.S., F.I.C.

(*Read at Meeting, November, 1888.*)

DURING the last six months the writer has been engaged in the production of soap-thickened oils. Correct determinations of melting points was a matter of the first importance, but the presence of soap rendered the ordinary methods of working impracticable. The melting points of many samples range far beyond the temperature of boiling water, and the effect of a heat much below the actual melting point is to cause the liberation of a small portion of the oil and entirely vitiate the results of either adhesion or gravitation processes.

Constant readings are obtained by operating as follows:—A clean narrow test-tube is fitted to a thermometer by means of a short length of hard rubber tubing. The space between the walls of the test-tube and the thermometer must not exceed the sixteenth of an inch. The test-tube is passed through a hole in a cork, and this fits the mouth of a wider and longer tube. A little of the sample to be tested is taken upon the bulb of the thermometer, which is then thrust carefully into the narrow tube to within half an inch of the bottom.

The whole arrangement is now suspended so that the wider test-tube is sunk to nearly its entire length in a beaker of clear lard oil. The beaker stands upon an iron plate over a Fletcher Argand lamp—a little manipulation of the gas supply ensures a gradual and regular rise of temperature. The tubes are brought up to the side of the beaker, so that the observation may be taken by aid of a hand lens. The true melting point is accepted as that at which the mass flows down to a clear bead at the bottom of the tube. The writer has obtained exactly concordant results with oils containing 20 per cent. of soap. The accompanying sketch will serve to make the details clear.



## THE PRESERVATION OF MILK SAMPLES.

By H. DROOP RICHMOND.

(*Read at the Meeting, November, 1888.*)

THE preservation of Milk Samples is most important to public analysts; a milk analysis must be commenced immediately on receipt of the sample, and after the analysis is finished it is not possible to check the results if required, nor should the analysis be disputed, can the sample be referred to another analyst.

Allen (*ANALYST*, XI., 203) has devised a process for the preservation of milk samples by means of alcohol, but as a large quantity of the preservative must be added, very much depends on the exactness of the proportions, and it is doubtful whether the analysis of a sample so preserved would be of any value in a law court.

It is, of course, apparent that as small a quantity as possible of the preservative should be added. Besides carbon bisulphide, and ether, which were used by Hehner, I have tried the preservative action of dichlorophenol, chloroform, terpenes, and hydrofluoric acid; none of these except hydrofluoric acid proved wholly satisfactory; chloroform, which kept the milk in a fluid state, and the fat in an easily miscible con-

dition, being perhaps the most unreliable; carbon disulphide kept the milks fluid, but allowed the cream to rise to form a cake at the top, which could not easily be mixed again; dichlorophenol preserved the milks fairly well, but the cream rose; ether and terpenes were of very little use; hydrofluoric acid, of which '5 per cent. was added, or one drop to 10 c.c. of milk, preserved the milks almost perfectly; of course it precipitated the casein, but a vigorous shake brought this into so finely a divided state, that sampling was quite easy, the fat being evenly mixed; there was not the slightest blackening of the total solids after preservation, showing that decomposition had not taken place; the fat was estimated by Adams' method (Thomson's modification), there being no difficulty in pipetting 5 c.c. on to a strip of paper, which absorbed it fairly well; in some cases it was necessary to add, after putting the milk on the paper, a few drops of ammonia, and to mix the milk and the ammonia with the stem of the pipette, which was afterwards wiped on a dry portion of the paper; the ash was taken in many cases before and after, and was found to have increased about '1 per cent.

A table of analyses is subjoined.

| No. | Days kept. | T. S. Orig. | T.S. Presvd. | Diff. | Fat Orig. | Fat Presvd. | Diff. |
|-----|------------|-------------|--------------|-------|-----------|-------------|-------|
| 1.  | 183        | 8.53        | 8.57         | + .04 | 2.27      | 2.21        | - .06 |
|     | 347        | "           | 8.57         | + .05 | —         | —           | —     |
| 2.  | 49         | 12.60       | 12.60        | —     | 4.16      | 4.07        | -.09  |
|     | 145        | "           | 12.32        | -.28  | —         | —           | —     |
| 3.  | 73         | 12.56       | 12.50        | -.06  | 3.58      | 3.53        | -.05  |
| 4.  | 45         | 13.36       | 13.17        | -.19  | —         | —           | —     |
| 5.  | 38         | 11.00       | 11.09        | + .09 | —         | —           | —     |
| 6.  | 39         | 11.56       | 11.50        | -.06  | 3.23      | 3.20        | -.03  |
| 7.  | 34         | 13.19       | 13.15        | -.04  | 5.24      | 5.27        | + .03 |
| 8.  | 34         | 13.24       | 13.35        | + .11 | —         | —           | —     |
| 9.  | 34         | 11.45       | 11.40        | -.05  | —         | —           | —     |
| 10. | 32         | 11.46       | 11.50        | + .04 | —         | —           | —     |
| 11. | 32         | 12.03       | 12.04        | + .01 | 4.03      | 3.96        | -.07  |
| 12. | 32         | 9.77        | 9.84         | + .07 | —         | —           | —     |
| Av. |            | 11.56       | 11.54        | -.02  | 3.75      | 3.71        | -.04  |

The whole of these milks were quite fresh when preserved; the following on the contrary were already three days old, when the hydrofluoric acid was added, and many had begun to turn—

| No. | Days kept. | T. S. Orig. | T. S. Presvd. | Diff. |
|-----|------------|-------------|---------------|-------|
| 13. | 30         | 12.97       | 12.82         | -.15  |
| 14. | 31         | 12.65       | 12.77         | + .12 |
| 15. | 31         | 14.56       | 13.84         | -.72  |
| 16. | 31         | 12.92       | 12.82         | -.10  |
| 17. | 31         | 13.33       | 13.27         | -.06  |
| 18. | 31         | 12.52       | 12.04         | -.48  |
| 19. | 32         | 12.30       | 12.55         | + .25 |
| 20. | 32         | 12.84       | 12.23         | -.61  |
| 21. | 32         | 12.51       | 12.65         | + .14 |
| 22. | 32         | 12.72       | 12.58         | -.14  |

These last samples were evidently decomposed, they smelt bad in many cases, were curdled in a much more lumpy state than the others, and in several fungus could be perceived.

In the first series, Nos. 1 and 2 after being analysed when preserved, were sealed up again, and kept for a further period; in both cases there was a blackening of the total solids, indicating that some decomposition had set in; this, and the facts that the ash increases, and that the total solids are not blackened when freshly preserved with hydrofluoric acid shows that the hydrofluoric acid disappears as such.

To further test this question a sample of milk was preserved when fresh; another portion was allowed to stand for three days, and then preserved; both samples were again analysed after the expiration of a fortnight, with the following results.

|  |        | T. S. Orig. | T. S. Preserved. | Diff. |
|--|--------|-------------|------------------|-------|
| 23. Milk fresh                                       | ... .. | 11.32       | 11.40            | + .08 |
| 24. After standing 3 days, without hydrofluoric acid |        | 11.07       | 10.70            | - .37 |

This shows that hydrofluoric acid only exercises a preserving action when added while the samples are fresh; if decomposition has commenced it is of very little use.

I would recommend that a portion of all milks it is desired to preserve, be taken on receipt of the sample, .5 per cent. of hydrofluoric acid be added, and the bottle securely sealed; no correction need be made for dilution of so small a quantity of liquid, as the difference is well within the experimental error.

The antiseptic power of fluorine compounds was pointed out by W. Thomson in a paper read before the British Association last year.

In conclusion, I must express my obligation to Mr. Hehner, in whose laboratory these experiments were carried out, for his advice and kindly interest in the work.

The Laboratory, 11, Billiter Square, E.C.

November 14th, 1888.

#### DISCUSSION.

Mr. DAVIES said he thought the suggestion was decidedly valuable. He would be glad to know whether by the statement that one-half per cent. hydrofluoric acid should be added to the sample it was intended to add the ordinary acid of commerce in this proportion, or such an amount of this solution as would give one-half per cent. true acid in the resulting mixture.

Mr. BLOUNT asked if the acid would have any corroding effect on the glass vessels employed?

Dr. VIETH said he was rather adverse to any tampering with samples, and it would be tampering if one-half per cent. of hydrofluoric acid or anything else were added. They would not like an inspector to add the acid, and if added, when the sample came into the hands of the public analyst it would have nothing to do with the sample kept for reference. He did not think a public analyst would recommend the addition of even a small proportion of acids.

Mr. HEHNER said that some time ago he brought some experiments before the Society and the same point was raised as to the desirability of preserving milk samples. No doubt it was very undesirable to give inspectors power to add anything to samples, and Mr. Richmond was adverse to that; but in the laboratory, and especially during the summer, it was much better in emergencies to be able to preserve samples without fear of their going bad than not to be able to do anything at all. He certainly thought that every sample which was condemned by the public analyst should be kept by him for reference. Not that portion which might go to Somerset House, as they had nothing to do with that, but their own sample should be preserved. He had seen all these experiments of Mr. Richmond's—the milk was curdled by the hydrofluoric acid—

but a good shake produced a perfect emulsion. There was no difficulty whatever in analysing it. In the experiments which he brought before them a year ago, in no case was the milk so old as those of Mr. Richmond's.

MR. RICHMOND in reply, said the hydrofluoric acid he used was the ordinary acid of commerce, and that he added .5 per cent. of that and not of the actual hydrogen fluoride. As regards Mr. Blount's question referring to the corroding effect of the acid on the vessels employed, he was not quite certain—if he meant had it any corroding effect on the glass bottles in which the milk was kept—he believed it had; but if he meant the porcelain basins used in the analysis, it had not. The weight of the basins after being cleaned out was exactly the same as before. As regards Dr. Vieth's objections, they had been answered by Mr. Hehner, with whose remarks he agreed.

[NOTE.—We have received the following from Dr. VIETH:—In the remarks which I made in the discussion on Mr. H. D. Richmond's paper "On the Preservation of Milk Samples," I have hardly done justice to this paper. Having fixed my mind upon one particular point, I must confess that in the discussion I lost sight of others. I am very strongly and most decidedly of opinion that official samples kept for reference should not deliberately be materially altered in their composition, not even for the sake of increasing their keeping qualities. But that does not exclude in other instances the employment of a convenient method for preserving milk samples in a state which allows their analysis to be deferred to a future time without interfering with the correctness of the results. Looking at Mr. Richmond's experiments, I freely admit that his suggestion, *i.e.*, preserving milk samples by the addition of a small definite quantity of hydrofluoric acid, is very valuable, and seeing that he has obtained exceedingly well-agreeing results in samples when analysed fresh and after having been kept for weeks, and even months, certainly one which is worth trying by analysts who in their private practice may receive milk samples with which they cannot deal at once.]

## ON SOME ABNORMAL SAMPLES OF BUTTER.

By ALFRED H. ALLEN.

(*Read at Meeting, December, 1888.*)

IN July last a sample of butter was condemned by a Public Analyst as being adulterated. The case was referred to Somerset House, and the chemists there, after enquiring as to the terms of the report of the Public Analyst, confirmed his certificate. The butter in question was shipped to England from Copenhagen, but was not of Danish origin, the dairy being that of Kjellstorp, near Wernamo, in Sweden. On learning that the butter had been condemned, the shipper sent a sample of butter from the same dairy to Professor V. Stein, the official analyst to the Danish Government. At the same time he took measures to have the dairy visited by the King's Bailiff and the British Vice-Consul, who went there and examined everything in and about the dairy, and also interviewed the owner and persons employed in the dairy, all of whom swore that no adulteration of the butter had ever taken place. In due course Professor Stein reported that the sample sent him contained so small an amount of volatile acids as to justify him in calling into question the genuine nature of the butter. At his request the King's Bailiff again proceeded to the dairy to see the butter made and to take samples of it. He watched the process of churning and working the butter in the presence of a representative of the British Vice Consul, and, as the result of the subsequent analysis, this sample of butter was found to have characters practically similar to those previously observed in the butter sampled in Copenhagen and in the butter condemned in England, some of which had been sent to Professor Stein. On learning the history of the sample of butter from the dairy, Professor Stein was led to doubt how

far the limits generally adopted by public analysts in the examination of butter were to be relied on.

The Royal Agricultural Society of Denmark, which, in many respects, acts as a branch of the Danish Home Office, now became fully alive to the importance of the question at issue, for Denmark being practically an enormous dairy-farm—a large proportion of the produce of which is sent to England—it was felt that the abnormality which had been observed in the case of the Swedish butter might very possibly extend to certain Danish butters, and hence it was very important to know the variations in composition which were natural to butter under exceptional circumstances. In support of this view, and at the suggestion of Mr. Harald Faber, Agricultural Commissioner abroad to the Danish Government, I was formally invited to visit Denmark, inspect thoroughly the whole process of the manufacture of butter at certain dairy-farms, and analyse the product obtained under these crucial conditions. Of course, it would have been impossible to visit and watch the process of butter-making at even a tithe of the numerous dairy-farms existing in Denmark, but the investigation was simplified by the fact that Professor Stein, who practically occupies the position of Public Analyst for the whole of Denmark, receives, under the Danish Margarine Act, three samples of butter daily, three inspectors being constantly employed in visiting the farms and taking samples of the products. Hence, Professor Stein was able at once to point to certain farms whence very abnormal butter had been obtained, and consequently our attention was specially directed to the product from these places. Accordingly, early in last month I visited Copenhagen, and met in conference at the Government laboratory Professor V. Stein; Professor Th. R. Segelcke, Lecturer on Dairy-products in the Copenhagen College of Agriculture; Mr. B. Büggild, Consulting Dairy Chemist to the Royal Agricultural Society of Denmark; and my travelling companion, Mr. Harald Faber, Commissioner Abroad of the Agricultural Department of the Danish Government. The following day we (with the exception of Professor Segelcke, and with the addition of Mr. A. Stewart MacGregor, British Vice-Consul at Copenhagen) proceeded to a distant part of Denmark, where was situated one of the farms ("B") already referred to. There we witnessed the milking of thirty-one cows, the product from each of which was weighed separately. The mixed milk was then put into a receptacle for ripening, and the lid securely sealed and fastened by Mr. MacGregor and myself. The next morning, having noted the conditions of the seals, we opened the vessel, and watched the transference of the contents to the churn. The usual addition of butter-colouring was omitted. The churning being completed, we watched the butter worked and placed in a number of tin boxes, which boxes were then put into strong linen envelopes, which were closed and sealed by Mr. MacGregor and myself. We then proceeded to another farm ("O"), where we saw sixty-five cows milked, and watched the manufacture of butter in the same jealous manner as before, the product being duly sealed as on the previous occasion. The milking of the cows, as well as the treatment of the milk and butter, was conducted at both farms under the unremitting supervision of the whole party, and especially of Mr. Macgregor and myself. I am, therefore, in a position to give a most positive guarantee that the samples of butter in question were absolutely genuine products.

The butter made at "B" farm was the produce from milk yielded by cows which had been in the stalls for six days, but which previously had been fed on grass land reclaimed from the sea. Most, but not all, of the cows were in calf, some being pretty far advanced, but others not expected to calve until May next. At "O" farm the cows had been longer in the stalls, but were all expected to calve within a few months.

I may say here that I was greatly struck with the extremely methodical manner in which the operations of milking and butter-making, and in fact the whole work of the farms, were carried out. Everything was scrupulously clean, and the whole manufacture was conducted on the most scientific principles, a thermometer being employed at every stage of the operation, the milk and other products weighed, and a definite proportion of salt added. It is impossible to conceive a manufacturing operation of the kind carried out in a more perfect, systematic, and cleanly manner, and it certainly is a matter of regret that many of our English dairies are so far behind those in Denmark.

On returning to Copenhagen, Professor Stein and I opened one of each of the sealed packets and jointly made an analysis of the contents. The method on which we placed the most reliance was Wollny's modification of the Reichert Process for determining the volatile acids," a translation of which by Mr. O. Hehner was published in the ANALYST last winter. The process as there described (Vol. xiii. page 40) is strictly that used by Professor Stein, but I may say that he lays special stress on the importance of ensuring the entire absence of carbonic acid. The water used is hot or recently boiled, and, by means of a T-piece in the tube by which the flask is connected with the condenser, the alcohol can be distilled off, and water added to the residual soap without opening the flask and so exposing the contents to the air. Another important point to which great attention is directed is to heat the acidulated liquid very gradually, and not to attempt to commence the distillation until the layer of fatty acids has become clear and the aqueous liquid has almost entirely lost its original milky appearance. The time of thirty minutes for the distillation of 110 c.c. is strictly adhered to, with a variation of not more than two minutes more or less.

My previous experience of Wollny's method, which I have used habitually for the analysis of butters ever since the appearance of the translation in ANALYST a year ago, had shown me that the results were very satisfactory, and, if anything, somewhat higher than those I used to obtain by the Reichert process as worked by myself, and described in my "Commercial Organic Analysis" (Vol. II. p. 45). The higher result is probably due to two or three causes. Thus, I had been in the habit of distilling off 50 c.c. out of 75, which is a smaller proportion than 110 out of 140. This difference probably more than compensated for any error caused by the presence of carbonic acid in the old way of operating. As worked by me, I do not think I ever lost volatile acids in the form of butyric ether, as I always used a flask fitted with a proper condensing arrangement. Professor Stein's experience of a number of samples of butter of known purity shows that, in his hands, and worked in the exact manner I have described, the volume of decinormal alkali neutralised by the volatile acids from 5 grammes of butter-fat ranges from 31.59 c.c. to 25.08 c.c. with an average of 28.64. I should myself have fixed the average at 28.00, or a little below it, so that our experience is fairly concordant in that respect.



The experiments on the samples of butter-fat in question, which were marked respectively "B" and "O," gave in Professor Stein's laboratory the following results:—"B" required 22.70 c.c. which, with the correction of 0.17 shown by a blank experiment, gives 22.53 c.c. as the final result. The butter-fat from the sample marked "O" gave a result of 24.76 c.c.

I may say that I took the most rigid precautions to avoid the introduction of any possible source of error—such precautions as might well have been resented by a brother chemist, had he not been well aware that their object was to meet all possible criticisms, and not because there was any real doubt in my mind respecting the conditions of working. Thus, I proved the accuracy of the weights of the balance employed; I personally took every weighing and measurement; I proved the neutrality of the distilled water, alcohol, and phenol-phthalein employed; I verified the capacity of the burette, pipettes, and measuring flasks; and I set the baryta solution. This was done by titration, with a sample of quadroxalate of potassium obtained from Professor Wollny, of Kiel. I brought some of this reagent home with me, and have since verified its substantial, though not absolute, accuracy, by titration against solutions made up in England. I have also made for myself some of this acid oxalate of potassium which has the formula  $\text{KHC}_2\text{O}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4 + 2 \text{ aqua}$ , and seems to offer certain practical advantages over oxalic acid, as it is of definite composition, easily prepared and purified, and not efflorescent. I have prepared it by making a saturated solution of re-crystallised oxalic acid in water and filtering the liquid. One-fourth of this liquid was then heated to boiling, and neutralised with pure potassium carbonate, employing litmus paper as an indicator of neutrality. This neutralised solution was then added to the main quantity, whereupon a copious deposition took place of the quadroxalate in the form of a granular powder. This powder is filtered off, washed with a little cold water, and dried over sulphuric acid. In using the quadroxalate for setting the baryta solution, about .25 of a grm. is exactly weighed and dissolved in a little warm water. Phenol-phthalein is then added and the baryta water run in until the pink colour becomes permanent. During the first part of the titration the solution remains quite clear, but subsequently a white precipitate of oxalate of barium is produced, and this forms an extremely delicate background for viewing the end of the reaction. In fact, I think it would be a distinct advantage in such titrations to aim at the presence of a finely-divided white precipitate in the liquid, rather than to employ a white background to the vessel. Of course, baryta possesses a manifest advantage for this purpose over caustic soda, for a clear solution of baryta must be free from carbonic acid, the presence of which affects any titrations in which phenol-phthalein is employed as an indication.

The time at my disposal in Copenhagen did not allow of any further analytical examination on the spot of the butter-fats in question, with the exception of the determination of the specific gravity of the sample marked "B." This was ascertained by a specific gravity bottle of a kind I have been unable to obtain in England. It was a conical bottle, furnished with a thermometer having a range of a few degrees above and below  $100^\circ \text{C}$ . There was also a second orifice, consisting of a vertical capillary tube ending at the top in a small funnel. The bottle having been filled with the butter-fat and the thermometer stopper inserted, it was immersed in a beaker of water, the tem-

perature of which did not rise more rapidly than  $1^{\circ}\text{C}$ . per minute, so that there was ample time for the contents of the bottle to acquire the temperature of the surrounding water. When an external thermometer shewed this to be at  $100^{\circ}\text{F}$ ., the fat which had passed by expansion into the little funnel surmounting the capillary tube was removed by means of filter paper, so that the measure of the fat was accurately adjusted to a mark just at the top of the capillary tube. The bottle was then removed and weighed with its contents, after which it was returned to the water and the heating continued, until the internal thermometer indicated that the fat had reached a temperature of  $100^{\circ}\text{C}$ . It was then removed and weighed as before. We had previously observed the weight of the bottle when dry and empty and when filled with water at  $15^{\circ}\text{C}$ . Hence the experiment gave us the means of ascertaining the density of the butter not only by Bell's method at  $100^{\circ}\text{F}$ ., but also at  $100^{\circ}\text{C}$ .

The following were the figures obtained, water at  $15^{\circ}\text{C}$ . being unity:—

Specific gravity of "B" butter-fat at  $100^{\circ}\text{F}$ . ( $=37.8^{\circ}\text{C}$ .) .9055.

" " "  $100^{\circ}\text{C}$ . ( $=212^{\circ}\text{F}$ .) .8639.

This gives an apparent expansion-coefficient of 0.00067 for  $1^{\circ}\text{C}$ .

In concluding the description of the experiments made at Copenhagen, I cannot omit to give expression to my sense of the great courtesy shown me by Professor Stein and his assistants, and my high appreciation of the methodical manner in which the work there is evidently done, and which is in itself so good a guarantee of its accuracy.

It must be remembered that in order to ripen the milk in time to allow of its being churned in twelve or sixteen hours after milking, it is necessary to add to it a certain proportion of buttermilk. Hence my critical examination of the butters in question would not have been complete had we omitted to analyse the butter-milk added, with a view of proving that it was not a medium of introduction of any foreign fat. The examination was made by rendering 100 c.c. of the butter-milk alkaline with ammonia and agitating with ether. The ether was allowed to separate and the agitation repeated with a fresh quantity of ether. The ethereal solutions were mixed and evaporated, the residual butter-fat being weighed. It amounted to barely 0.1 per cent. of the butter-milk, and hence even had the fat so extracted consisted wholly of foreign fat, it could not have appreciably affected the results of the analysis. As a matter of fact, however, we made an observation of the index of refraction of the extracted fat by means of Abbé's Refractometer, and found it to be 1.4620—a result which agrees with that of genuine butter-fat. I may here say that this is my first experience of the use of Abbé's Refractometer, which Professor Stein informs me is capable of distinguishing with certainty butter from other fats, but is not of much service for mixtures containing butter.

I brought away with me some of the sealed packets containing samples of the butter in question, while others were left with Professor Stein and Mr. Faber. I also brought a portion of the butter-fat rendered from the butters in question in Professor Stein's laboratory. Since my return to England I have analysed these samples of butter-fat as well as the butters brought home in their original condition, and have not limited myself merely to the Reichert-Wollny process, but have examined them by other well-known processes.

My results are as follows:—

|  | B.                     |                        | O.                     |                        | N.                                   |
|--|------------------------|------------------------|------------------------|------------------------|--------------------------------------|
|  | Butter-fat Rendered in |                        | Butter-fat Rendered in |                        | Average butter-fat<br>from V. Stein. |
|  | Copenhagen.            | London.                | Copenhagen.            | London.                |                                      |
| Specific Gravity at 100° C. . . .                                      | ·8639                  | ·8640                  | ·8641                  | ·8641                  | ·8653                                |
| Decinormal Alkali by Reichert - Wollny Process . . . .                 | 22·63                  | 22·39                  | 24·39                  | 24·70                  | 29·2                                 |
| Percentage of KHO required . . . .                                     | 22·27                  | 22·05                  | 22·15                  | 22·03                  | 22·67                                |
| = Saponification Equivalent . . . .                                    | 251·9                  | 254·4                  | 253·3                  | 254·6                  | 247·4                                |
| Soluble Fatty Acids, per cent. . . .                                   |                        | { 4·37<br>4·50<br>4·45 |                        | { 4·60<br>4·66<br>4·77 | { 5·52<br>5·54                       |
| Reichert-Wollny on Soluble Acids . .                                   |                        | 22·76                  |                        | 24·70                  | 28·96                                |
| Insoluble Fatty Acids per cent. . . .                                  |                        | { 90·24<br>90·62       |                        | { 89·90<br>90·30       | { 88·47<br>88·49                     |
| Melting Point of Insoluble Acids ° C                                   |                        | 36·5                   |                        | 39·0                   | 41·0                                 |
| Turbidity - temperature; Acetic Acid Test:— Genuine Butters 62-63° . . | 74·5                   | 75·0                   | 72·5                   | 73·0                   | 68·5                                 |

Before proceeding to the discussion of the other results, some explanation is required respecting the above determinations of specific gravity. The figures quoted are calculated to a temperature of 100° C., though actually observed at a temperature of 99·5° C. The coefficient of expansion of butter-fat according to the experiment already recorded being ·007 for 1° C., it follows that the gravity of, say "N" sample at 99·5° was ·86535, and similarly the other observations were ·00035 higher than the figures recorded in the tables.

In my work on "Commercial Organic Analysis," Vol. II., I state the average specific gravity of butter-fat as being 0·868 at 99°, equivalent to ·8673 at 100°. This determination, like nearly all the other densities of fats at 100° C. published by me, was obtained by the means of a Westphal balance. The accuracy of this had been ascertained by comparing the gravities of proof-spirit and milk shown by it with determination of the gravities of the same samples made by the specific gravity bottle, and the accuracy of the rider weights was also verified—a precaution which was by no means

unnecessary, as one of the riders was found to differ very seriously from its supposed weight. Very recently I was struck with certain differences in the determinations of densities of butter, lard, and other fats at the boiling point of water when made by the plummet and by the specific gravity bottle or Sprengel-tube, and for some time was wholly at a loss to account for the discrepancy, which, however, has now been definitely traced to the faulty division of the beam of the Westphal balance. The instrument I used was one purchased of a London firm that has supplied a number of instruments in this country. Mr. W. Chattaway, who discovered the nature of the error, has examined all those in stock at present, and finds the error common to all, and therefore very probably it exists in all or most similar instruments in use in England. The fault consists in the notch at the eighth division of the beam being sensibly nearer the fulcrum than it should be. The effect of this is evident. All weights placed on the eighth division do not exert their full leverage, and additional weights have to be added to effect the counterpoise. In the case of my instrument, the error can be readily detected with a fine pair of compasses, and is even visible to the unassisted eye of some observers when their attention is directed to the point. The consequence is that the greater number of the determinations of gravity, commencing with .8, including all determinations of specific gravities of butter, lard, and other fats at 100° made and published by me up to a very recent date, have been in excess of the truth by about .0015. Hence the statement in my book that the average density of butter at 99° is 0.868, should be modified to  $0.8665 = 0.8658$  at 100°. The discovery of the error in question would have been made long ago had the balance been checked against the specific gravity-bottle with rectified spirit instead of proof spirit and milk. The history of it I have given will serve as an illustration of the ease with which an error may creep into absolute determinations, and hence how difficult it is for chemists to compare strictly their own results with those obtained in other laboratories. Of course all my results are strictly comparable among themselves, so that the error has not affected any conclusion arrived at; but I think it right to place the fact on record, as I believe other chemists are likely to be obtaining erroneous figures from exactly the same cause. One other practical conclusion may be deduced from my experience, and that is, that the rider system is open to grave objections when applied to the larger weights of a balance.

With regard to the determination of the saponification equivalent and of the soluble and insoluble fatty acids, I have nothing to say, except that the highest estimations of insoluble acids were obtained in experiments in which the washing was known to be carried out less perfectly than in the other cases.

The turbidity-temperatures by the acetic acid test were made by heating 3 c.c. of the melted butter-fat with its own measure of glacial acetic acid until the mixture was clear, and then stirring with a thermometer until the liquid became turbid throughout. The test-tube in which the experiment is conducted should be immersed in an empty flask, so as to avoid too sudden cooling and the effects of currents of air. I have now used this test for several years with very satisfactory results. It enables butter to be distinguished from other fats with the utmost facility, and in the case of samples of genuine butter, the temperature at which turbidity occurs closely follows the other characters of the butter; that is to say, a butter rich in lower fatty acids, and therefore giving a high result by the Reichert-Wollny test, will give a low turbidity-temperature by the acetic acid test. Repeated experiments on the same samples give results which are concordant within 1° C. The strength of the acetic acid used affects the test in an enormous degree; in fact, I fancy the solubility of a definite fat in glacial acetic acid would be the best possible test for the strength of such acid. A sample of acid which when used for testing genuine butter will show a turbidity-temperature of 60° C. will show with butterine a turbidity-temperature of 100°, but by putting a very small

proportion of water to such acid the temperature of turbidity is so raised that the results of the butter-test will be like those given in the table. Hence, in order that the results may be comparable, it is necessary to define in the strictest manner the strength of acid used, and this is somewhat difficult to do. The acid I employed for the experiments quoted above had a specific gravity of 1.0563 at 15.5° C., and when titrated with standard baryta water and phenol-phthalein, was found to contain 95.14 per cent. of real acetic acid ( $C_2H_4O_2$ ).

From a careful consideration of the foregoing experiments, it appears that the butter in question marked "B" had a density quite outside previous experience of genuine butter-fat, and by analysts relying much or exclusively on this indication would be very liable to be condemned as adulterated. The volume of alkali required by the butter when examined by the Reichert-Wollny process was sensibly below the limit hitherto recognised. The saponification-equivalent was at or beyond the extreme limit hitherto observed (253). The proportion of soluble fatty acids was lower than has been observed in any previous genuine butter, except some analyses of doubtful accuracy. The insoluble fatty acids are sensibly in excess of those previously observed; the highest figure recorded by Dr. James Bell in a butter not altered by keeping being 89.9 per cent. The foregoing remarks apply, though somewhat less strongly, to the sample marked "O." Before leaving this part of the subject, I may say that I have on the table a further quantity of the butters in question contained in the original sealed packets. I have permission to place them at the disposal of any Public Analyst who will undertake to examine them fully and communicate his results to me.

Although the Danish butters which yielded me the abnormal results already described are of exceptional character, we must remember that they really represent the butter produced from the mixed milk of a large number of cows, which were yielding much the same kind of butter a year previously, and in the face of these facts, and of the Swedish experience already recorded, it cannot be said that such butter may not be met with in practice.

My attention has been called by Mr. Faber to some experiments made by Adolph Meyer, published in the "Milch-Zeitung" for October 17. These relate to the butter produced by a particular cow which, according to Meyer, yielded milk the butter-fat of which had the following characters.—

|                     | Specific gravity at 100°. | Volatile acids c.c. |
|---------------------|---------------------------|---------------------|
| 1st Hay period      | .8632                     | 29.5                |
| 2nd " "             | .8627                     | 27.1                |
| 1st Ensilage period | .8621                     | 26.4                |
| 2nd " "             | .8620                     | 20.2                |
| 1st Mangold "       | .8640                     | 32.4                |
| 2nd " "             | .8629                     | 28.2                |

Meyer states, however, in a foot-note, that the specific gravity figures are merely comparative, not absolute; so that the results have less value than would otherwise have been the case.

Nilson, of Stockholm, again, in experiments made in 1886 by the unmodified Reichert process, found the volatile acids to vary materially with the length of time since calving. While very low at first, requiring only about 10 c.c. (+2=20 for 5 grms.) of alkali for their neutralization, they rose to a maximum in about a week, and maintained this high figure for about four weeks, after which they fell gradually to about 12 (=24), but only very rarely below that figure.

The produce from single cows may, of course, be expected to vary still more than that from a number of animals, but in practice there must be very little butter sold

which is the produce of only one or two animals, and the milk of a normal cow being usually much larger in quantity than that of an animal yielding an abnormal product, the variations from the mean composition in the case of united milk is not likely to be great.

A very great object would be gained, if we could trace a sample of butter back to the farm and cows which produced the milk, and I think we should look forward to the day when an alteration of the law will render this possible.

Although the results I have recorded undoubtedly show that butter-fat varies in composition more than was supposed, and will render the detection of adulteration decidedly more difficult in cases where a moderate percentage of foreign fat has been added, I do not think we have yet come to the end of our powers in butter analysis. The detection of cocoanut oil, which I met with in one sample of butter in considerable amount, can be effected with certainty, by the large yield of solid volatile acids and their peculiar odour. Besides, the specific gravity of the butter is rather increased than diminished by the presence of cocoanut oil. Cotton-seed oil will indicate its presence in more than one way. Seeing that all margarine now-a-days contains cotton-seed or other vegetable oil, it is worth while to try and detect their presence. The isolation of phytostearin, or vegetable cholesterol, might possibly afford a test for vegetable oils, as suggested by Mr. Hehner with respect to lard. Some modification of the chloride of sulphur test may be found available, while cotton-seed and most vegetable oils might be indicated by the increased iodine-absorption of the sample or of the oil separated from it by pressure. In such expressed oil, earthenut oil might possibly be recognised by isolating arachidic acid, while sesame oil can be detected by the sugar reaction even in the original sample. The chemistry of the vegetable oils is still imperfectly understood, and researches in this direction would almost certainly lead to the discovery of new methods of detecting them. Hence, we ought to aim at a further advance in our methods of examining butter, rather than remain content with processes which, however good and ingenious in their way, do not give us all the information we require.

Professor Wollny, of Kiel, has requested nearly thirty chemists to assist him in ascertaining the natural variations in analytical characters of butter-fat, in order to render the results more strictly comparable. He has published and circulated a printed description of the exact method to be employed in the analysis, together with forms on which the results are to be tabulated. To give an idea of the field proposed to be covered by the scheme, I may quote the following data with which Dr. Wollny requests each analyst to furnish him:—The strength of the sulphuric acid with which the baryta solution is set. The number of c.c. of baryta used for neutralisation. The strength deduced from this result, and the strength of the baryta solution deduced from its titration by acid oxalate of potassium. In estimating the volatile acids, the result of a saponification with and without alcohol. The time of each distillation, and blank analyses in each case. The mean molecular weight of the volatile fatty acids (distilled from their magnesium and copper salts). The volume of baryta solution neutralised by the acids soluble in boiling water and in 10 per cent. alcohol. The percentage of insoluble acids, by washing on the filter and by washing in a current of steam; and their mean molecular weight. The percentage of free fatty acids in the butter-fat. The saponification-equivalent of the fat. The molecular weight of the total fatty acids. The iodine absorption. The refraction index of the butter-fat; and, for comparison, of olive oil, nitrobenzene and alpha-monobrom-naphthalene. The special gravity at 0° or 15° and at the temperature of boiling water, by the specific gravity bottle, plummet method, and hydrometer. These determinations, with the melting point and solidifying point of the fat, seem a tolerably complete examination. It would be impossible, even were it desirable, for our Society to institute any series of experiments of the same wide-

reaching character; but it occurs to me that we might with advantage appoint a small committee to receive and tabulate results which might be communicated to them by members of the Society, and to devise, if possible, some method of examining butter which should be less dependent on the natural variations in its composition than the methods at present in use.

In conclusion, I desire to express my indebtedness to Mr. Faber for his good offices as interpreter and travelling-companion, and to Mr. Wm. Chatterway for the zeal and care with which he has executed many of the determinations, the results of which I have recorded.

#### DISCUSSION.

DR. VIETH (who had temporarily taken the chair) said they would all agree with him that the question Mr. Allen had brought forward was of the greatest importance to public analysts. Personally, he was very pleased to see that Mr. Allen had not only taken the trouble to see the butter made, but had seen the cows milked and the milk locked up, so that no hitch could occur similar to that which happened in the case of the Swedish dairy in which the butter was produced, which was the cause of the investigations dealt with in Mr. Allen's paper. In this case the Government's officers only saw the cream churned, and had taken no precaution to put the purity of the cream beyond doubt. Next to milk, butter had given them perhaps the greatest amount of trouble lately.

As regards the requirements of the German Commission which had been mentioned, he should like to add that, not only one, but five determinations of each kind were to be given, and this, of course, caused a great sacrifice of time. Had Mr. Allen made any experiments as far as regarded the distilling off of the volatile fatty acids? Wollny and Stein laid much stress on the fact that distillation should not be proceeded with too quickly, but that the fatty acids should be melted first, and the aqueous liquids allowed to become clear. What difference would it make if they proceeded a little more quickly, and did not wait for the clearance of the aqueous liquid? As far as his experience went he did not think there was much difference. He had found that the butter sent to the members of the German Commission, which was produced at Kiel in July, required about 30 c.c.  $\frac{N}{10}$  alkali—Reichert-Wollny—while a number of samples of French and Danish butters, examined during the last weeks, required from 25 to 26 c.c.

Mr. HARALD FABER said—It is not to be denied that the proved existence of genuine butter of such an abnormal composition as those mentioned by our president interferes very seriously with the detection of mixtures of butter with foreign fat, and it might therefore seem peculiar at first that an exertion has been made on behalf of the butter producers in Denmark, being very far from interested in mixtures, to put such a check on the control of butter. But I think the position of the Royal Agricultural Society of Denmark to this matter is very clear. A recent case, which Mr. Allen mentioned, proved what risk we run by leaving matters as they were. I wish to point out that we have in no way questioned the correctness of the English analyses of the butter sampled in Wigan and condemned as adulterated; but having had the opportunity of examining samples from the dairy from which the butter in question originated, and some of the butter fat rendered from the official duplicate sample, and having learned already last year that genuine butter can be produced of still more abnormal composition than the butter in question, we expressed the opinion that the fact of this butter having such a composition was not sufficient proof of its being adulterated. But our assertion that genuine butter might be of such a quality that English analysts would call it adulterated was, perhaps, not likely to be taken notice of without further proof. Knowing that some day genuine Danish

butter might be condemned here as adulterated if no step was taken, two courses were open to us—either to leave matters as they were, which meant running the risk of losing the well-merited name as producers of first-class and genuine butter, or to prove the existence of the abnormal butter, and then, perhaps, have to compete still more with mixtures from other countries, which would then be more difficult to detect. I urged the adoption of the latter course, which was finally agreed to, and we have all reason to be well satisfied that Mr. Allen, at our invitation, undertook the long journey to Denmark, and also with the excellent work he has done. The way in which these abnormal butters were first found is as follows:—As it has been said, Prof. Stein is the Public Analyst for the whole of Denmark, which is equivalent to about half of London as regards population. He received in 1887 some samples of butter of which he at first felt convinced that they were mixtures. He therefore ascertained the names of the farms from where they originated, and he had samples taken with all guarantee of purity, and in that way found that in September, 1887, some large farms in Denmark, with large herds of milch cows, gave butter which yielded below 25 c.c., by Reichert-Wollny, one even as low as 21.7, another 21.9. His experience in butter analysis is now, as mentioned by Mr. Allen, very extended, having three samples a day from our inspectors under the Margarine Act. Whenever a sample of doubtful character has been taken at a dairy, a warehouse, or a shop, the inspector is sent at once to the dairy where the butter was produced, to obtain an authentic sample. In this way it has been found that butter of this abnormal character may occur at different farms, but, as it seems, for a very limited period only. The lowest figure by the Reichert-Wollny test yet found in butter-fat from a herd is, as far as I know, 21 c.c. It is only this extended experience of Prof. Stein's that enabled him to pick out a farm where we could invite Mr. Allen to go and take samples, and it was only done with great difficulty. Some of the farms where the butter had been abnormal in September, 1887, gave October of this year butter in every respect normal, others gave abnormal butter when first tested, but when the test was repeated a week later, the butter was good again. It was very much of a chance that we hit on a farm yielding butter of a description like the sample "B."

I have been informed by my friend Dr. O. Hehner, that Prof. Besana, in Italy, has proved the existence in Italy of genuine butter of the same abnormal condition. He found amongst 114 samples 2 yielding between 21.8 and 22 c.c. by the Reichert-Wollny process, 1 yielding between 23 and 24, 2 between 24 and 25. It may, therefore, reasonably be expected that such abnormal butter may occasionally be produced even in other countries. It seems happily to be rare exceptions, and this in a double meaning. Not only are such butters met with only on a few farms, but they are found there only at certain times. The reason of this peculiar quality of the butter cannot be given yet; but two circumstances at least seem to have some effect on the percentage of volatile acids. One is, the condition of the field or meadow, another, the distance from the time of calving. Very poor grass land may have the effect, but grass on reclaimed land, although it could by no means be called poor, neither the land nor the grass, and although the grass was plentiful, have in some cases been considered the cause of the low contents of volatile acids in the butter. As far back as 1886, Prof. Nilson, of Stockholm, experimenting on a large number of single cows, found that the contents of volatile acids varied with the distance from the time of calving; on the first days the contents was very low indeed—10 c.c. by the old Reichert test; in about a week it reached a maximum, where it remained for a few weeks, when it gradually fell towards the end of the time of lactation. In this connection it will be of some interest to learn that the cows on farm B which gave the most abnormal butter had, until some days before the samples were taken, been on grass on reclaimed land of good quality. They were most of them in calf, but with a variation



in time till their next calving of 5 months; while the cows on farm O were all very near to their next calving, and consequently more late milking, but they had not been on reclaimed land.

It ought to be mentioned that low contents of volatile acids seems to stand in no relation whatever to the commercial value of the butter.

MR. HEHNER said that the facts brought forward by Mr. Allen were, without doubt of far-reaching importance. Public analysts would have to acknowledge that exceptional samples of butter did occur which would analyse like mixtures containing about 25 per cent. of margarine. If only one such exceptional sample occurred in every hundred, as there was some evidence from the Italian experiment quoted by Dr. Faber, it would yet be henceforth impossible to give a satisfactory opinion on any sample which contained less than 25 per cent. of foreign fat. Such an acknowledgment would result in immense injury to the public and the butter trade; It therefore behoved public analysts at once to set to work to find out the cause of the extraordinary discrepancy, less in the physiological direction, or regarding the food or other circumstances influencing the cows, but in a chemical direction. The question had to be solved: In what points does a natural abnormal butter differ from one adulterated with, say 25 per cent. of foreign fat? He was convinced that there were such differences, and he drew, in this direction, attention to the following facts, deducible from Mr. Allen's analysis. On calculating from the Reichert results the percentage of volatile acids as butyric acid (although, of course, the totality of volatile acids is not obtained by distillation), there in normal butters almost reached the soluble acids estimated in other ways. Thus, in the "normal" butter of Mr. Allen, butyric acid, by Reichert, 5.14 per cent. soluble fatty acids, 5.54 per cent., or 93 per cent. of the total soluble fatty acid obtained by distillation. In sample O, which would be passed as genuine upon the Reichert results, 4.34 per cent. were obtained by distillation, against 4.66 total soluble acids, or also 93 per cent. But in sample B, which was quite abnormal, only 87 per cent. of the soluble acids were volatile.

These figures seem plainly to indicate that, in this particular abnormal sample at least, the breaking down of the albuminous matter from which butter-fat in all probability results, was not so complete as to form butyric acid, but other acids slightly higher up in the fatty series. This conclusion, he thought, was confirmed by an observation of his (Mr. Hehner's) upon the abnormal sample, a portion of which had been given him by Dr. Faber, namely, that towards the end of the distillation, notable quantities of solid fatty acids congealed in the condenser, similarly as in the case of cocoa-nut oil.

It appeared to him to be of the highest importance now to direct our attention to the intermediate fatty acids, and he had no doubt that thus this difficulty might be overcome. The German Committee would thoroughly investigate the methods at present at our command, and it was not necessary to work in this direction; he would, however, suggest that, unless Mr. Allen was prepared to take personally upon himself the immense labour of carrying out an investigation such as he (Mr. Hehner) had indicated, it would be well that the Society should appoint a Committee upon whom the labour would devolve.

MR. ALLEN said in reply that the question was quite a different one from that submitted to the Milk Committee. In the latter case they knew what they wanted, and their object was to devise a method which would give accurate and reliable results in the hands of a number of chemists. In the present case they did not know exactly in what direction to look for success. It was a question of studying more closely the composition of butter as compared with other fats. He had already indicated certain directions in which hopeful work might be done, and he was thoroughly in accord with Mr. Hehner in his suggestion regarding the desirability in future of differentiating the

fatty acids more thoroughly than had been done in the past. In fact, he had suggested that direction, as a desirable one in which to work, to Mr. Faber, only a few days ago. His proposal was, that a small committee should be appointed to consider whether they could not devise some other process of examining butter for foreign fats. He did not personally know how far the results were affected by the time of distillation, and by neglect of the precaution to allow the fatty acids to become thoroughly molten before commencing to distil. Professor Wollny had recorded a number of experiments on this point, and, it being an arbitrary process, he had thought it his duty to follow the manipulation prescribed by Wollny as closely as possible, especially as the requirements were so easy to comply with. In conclusion Mr. Allen said that he was personally extremely sorry that the experiments on the Danish butter had turned out as they had done. He would have much preferred that they should have established the constancy of the composition of butter-fat rather than its variation beyond the accepted range of composition. But public analysts must not rest on their oars, but at once set to work to solve in a satisfactory manner the new problem raised by the experiments in question, and he had no doubt of their ultimate success. They must remember that a dozen years ago, before Messrs. Angell and Hehner devised their well-known process, they had no reliable method of detecting foreign fats in butter at all. He thought they should all combine for the purpose of overcoming the present difficulty, and he therefore proposed "That a Committee, consisting of the President for the time being, Dr. Vieth, Mr. Hehner, Mr. Faber, and himself, with power to add to their number, be appointed to consider and report on the possibility of improving the methods of analysing butter for the detection of adulteration." He relied on Dr. Vieth and Mr. Faber, not only for their great experience in the analysis of butter and other dairy products, but because they were, doubtless, in a position to obtain samples of which they knew the exact history, as regards the number of cows from which they were derived, the method of feeding, and so forth. The motion was seconded by Mr. Stokes, and carried after a short discussion.

*(Conclusion of the Society's Proceedings.)*

## ON SOURCES OF ERROR IN DETERMINATION OF NITROGEN BY SODA-LIME, AND MEANS FOR AVOIDING THEM.

By W. O. ATWATER.

*(Continued from page 237.)*

### *Loss by Dissociation and Oxidation of Ammonia.*

It is frequently urged that in the determination of nitrogen with soda-lime, ammonia may be dissociated at the temperature at which the combustions are conducted, and that in aspirating air through the tube at the end of the operation some of the ammonia may be burned. The following experiments were made in the hope of getting light upon the conditions under which such loss may thus occur in determinations as ordinarily made.

For this purpose means were taken to test the effects of (1) unusually long exposure of the ammonia to heat, (2) very high heat, and (3) exclusion of air. Ammonia was furnished by ammonium sulphate in which the ammonia had been determined by distillation by the method described by Gooch, two determinations giving respectively 21.11 and 21.14, and averaging 21.13 per cent. of nitrogen. About 0.3 gramme mixed with from 0.5 to 1.0 gramme of oxalic acid previously proven to be free from nitrogen were employed in each of the determinations detailed beyond. The soda-lime, made from 1 part of caustic soda and  $2\frac{1}{2}$  of lime, and the method of charging the tube, were as previously described. The method, which is that usually followed in this laboratory, involves filling the tube quite full of soda-lime, so as to avoid large open spaces which

become filled with gases and allow long sojourn of ammonia in the tube. Where the long tubes were used, the length of the anterior layer of coarse fragments of soda-lime was increased with the length of the tube, the length of mixture of soda-lime and nitrogenous substance and the charging otherwise remaining the same as in the tubes of ordinary length. The time of combustion, about thirty to thirty-five minutes, was naturally a little less than would usually be the case with animal tissues. The flames were turned off at the close of the combustion before the aspiration with air to wash out the ammonia. In No. 10 (see Table II.) the air was expelled before the combustion, and the ammonia washed out at the end by carbonic acid. In Nos. 11 to 19 the expulsion of air and cleaning out of ammonia were effected by a current of hydrogen, which was delivered by a generator so arranged as to permit easy regulation of the flow. The hydrogen was passed over heated copper foil, to remove the oxygen, before entering the combustion tube.

TABLE II.

*Determinations of Nitrogen in Ammonium Sulphate under Different Conditions.*

| By distillation, 21.11 and 21.14, average 21.13 per cent. |     |                      |         |                    |                           |          |                     |
|---|-----|----------------------|---------|--------------------|---------------------------|----------|---------------------|
| By Soda-lime.   |     |                      |         |                    |                           |          |                     |
| Series.   | No. | Length of Tube, c.m. | Heat.   | Aspirated with.    | Nitrogen found. Per cent. |          |                     |
|   |     |                      |         |                    | Separate Determinations.  | Average. | Range of Variation. |
| 1st   | 1   | 42                   | Medium. | Air.               | 21.12                     | 21.12    | .03                 |
|   | 2   | 42                   | "       | "                  | 21.10                     |          |                     |
|   | 3   | 35                   | "       | "                  | 21.13                     |          |                     |
| 2nd   | 4   | 75                   | "       | "                  | 21.11                     | 21.12    | .01                 |
|   | 5   | 75                   | "       | "                  | 21.12                     |          |                     |
|   | 6   | 75                   | "       | "                  | 21.11                     |          |                     |
|   | 7   | 75                   | "       | "                  | 21.12                     |          |                     |
| 3rd   | 8   | 75                   | High.   | "                  | 20.80                     | 20.83    | .06                 |
|   | 9   | 75                   | "       | "                  | 20.86                     |          |                     |
| 4th   | 10  | 75                   | "       | Carbonic acid.     | 20.91                     | 20.83    | .21                 |
|   | 11  | 75                   | "       | Hydrogen and pump. | 20.70                     |          |                     |
|   | 12  | 75                   | "       | " "                | 20.81                     |          |                     |
|   | 13  | 75                   | "       | " "                | 20.84                     |          |                     |
|   | 14  | 75                   | "       | " "                | 20.90                     |          |                     |
| 5th   | 15  | 75                   | Medium. | " "                | 21.10                     | 21.11    | .03                 |
|   | 16  | 75                   | "       | " "                | 21.10                     |          |                     |
|   | 17  | 75                   | "       | " "                | 21.12                     |          |                     |
|   | 18  | 75                   | "       | " "                | 21.11                     |          |                     |
|   | 19  | 75                   | "       | " "                | 21.13                     |          |                     |

(To be continued.)

## MONTHLY RECORD OF GENERAL RESEARCHES INTO ANALYTICAL CHEMISTRY.

PURIFICATION OF SULPHURIC ACID FOR KJELDAHL'S PROCESS. G. LUNGE. *Zeitschr. f. angew. Chemie*, No. 23.—Meldola and Moritz recommend to heat 10 c.c. of the acid for about two hours with .05 grm. of potassic nitrite. They take it, therefore, for granted that the nitrogen contained in commercial acid is always in the form of ammonia. The usual impurity is, however, nitrosylsulphuric acid, which the manufacturer tries to destroy by addition of ammonium sulphate. The decomposition is, however, never complete, so purified acid generally contains both nitrosylsulphuric acid and ammonia. The author criticises their method, which may give good results if the amount of ammonia is known and the theoretical amount of potassic nitrite is added, but which fails if any notable excess of nitrite is used. Then it is a great error to suppose that nitrous acid is completely expelled on boiling. Meldola and Moritz have overlooked the fact that the very stable nitrosylsulphuric acid is formed, which is but sparingly volatile. This fact is so well known that further experiments seemed almost superfluous, but to contradict the work of such an analyst as Meldola the author had several experiments carried out. A preliminary trial showed that .2255 grms. of sodium nitrite dissolved in 100 c.c. pure sulphuric acid gave a very strong nitric reaction after the acid had been boiling for two hours. A quantitative experiment was then conducted; .392 grms. of sodium nitrite was dissolved in 250 c.c. of pure sulphuric acid of 1.84 sp. gr., and 50 c.c. of this mixture diluted and titrated with permanganate, which showed a total of .1764 nitrous acid. The remaining 200 c.c. were now boiled for four hours, which caused 100 c.c. to distil over. The residue was now titrated, and showed a total of .175 grms. nitrous acid. The greater portion of nitrous acid was therefore still present. A second experiment gave before boiling .1938, after boiling .1842 grms. of nitrous acid. These experiments conclusively show that the purification process proposed by Meldola and Moritz is absolutely useless, and only then of avail when the quantity of ammonia is accurately known, so as to regulate the quantity of the nitrite. But in this case the simplest way is really to deduct this quantity (if not too large) from any quantity found during an analysis.

L. DE K.

DETERMINATION OF NITRATES IN WATER. S. C. HOOKER. *Berichte*, Dec. 10, 1888.—The author makes use of the property of the solution of carbazol in conc.  $\text{H}_2\text{SO}_4$  of turning deep green on the addition of small quantities of oxidising agents. The reaction is delicate enough to detect nitric acid in water containing one 2-millionth part of this substance. The following is the method used: A measured quantity of the water, 2 ccm. or less, is mixed with 4 ccm. of conc.  $\text{H}_2\text{SO}_4$ , and after cooling, a small quantity of carbazol in conc.  $\text{H}_2\text{SO}_4$  added. The colouration is compared with that obtained with varying quantities of  $\text{KNO}_3$  solution treated in exactly the same manner. A more detailed publication is promised.

A. L. G.

## MONTHLY RECORD OF ANALYTICAL RESEARCHES INTO FOOD.

**RIGHT-HANDED POLARISING HONEY.** VON LIPPMAN. *Zeitschr. f. angew. Chemie*, No. 22.—The author confirms the idea of Benseman (see ANALYST, 1888), and finds that when in the neighbourhood of sugar-refineries bees swarm there in their thousands, and regale themselves on the sugar. Their honey is then very clear and thin, but almost without the valued aroma. Four samples of such honey, analysed by the author, contained respectively 4·88, 3·92, 16·38, and 9·93 per cent. of saccharose. Samples showing such percentages cannot, therefore, be legally called adulterated. L. DE K.

## INFLUENCE OF DIFFERENT CATTLE FOODS ON THE COMPOSITION OF BUTTER.

**A. MAYER.** *Landw. Vers.*, 35.—The author has made a series of experiments to ascertain the composition of butter, and has arrived at the following conclusions:—  
1. There is a close relation between the specific gravity of butter-fat and the percentage of volatile acids. An increase in the one gives an increase in the other. 2. The melting point of the fat is not much influenced by the tributyrin, as it chiefly depends on the amount of triolein. 3. The amount of volatile acids in the butter of the milk of any particular cow is not so constant as was formerly believed, but is influenced by the quality of the food the cow has been fed on. 4. The amount of volatile acids is gradually increasing during the period of lactation. 5. When the food greatly consists of mangelwurzel the butter shows the highest percentage of volatile acid. Grass and clover will cause a larger amount than ensilage. 6. Hay and ensilage will cause the butter to have a high melting point, whilst green fodder will cause the lowest one. Mangelwurzel gives an intermediate melting point. 7. The solidifying point rises or falls with the melting point. 8. Cattle grazing in the fields will give the best milk and the richest butter. The author finds the quantity of deci-normal soda wanted for the distillate of 5 grms. of butter to vary from 20 to 30 c.c. L. DE K.

**THE OCCURRENCE OF BORIC ACID IN WINE.** GEORGE BAUMERT. *Ber.*, Dec. 10th, 1888., p. 3290.—The author's attention was drawn to this subject by his finding boric acid in every sample of a number of Californian wines analysed by him three years ago.\* Recently, Professor Rising, in San Francisco, stated that boric acid is a characteristic constituent of all Californian wines.† Soltsien‡ found that boric acid is a very frequent constituent of wines, and also occurs in cultivated and wild vines (*Ampelopsis quinquefolia*) in Saxony, whilst Ripper§ not only found it in 1,000 samples of German and other wines, but also in various parts of different kinds of vines. In one case he separated it as fluoboride of potassium from 2l. of a Riesling wine. The author has, for three years, tested every German, French, and Spanish wine which came into his hands, and found boric acid in them all; and also in must (fresh juice) from the Freyburg and Naumburg districts. He also systematically examined the growing vines in Thuringia in Saxony, and invariably found boric acid in the leaves, tendrils, wood, grapes, and grape-stems, examining 0·2 to 0·4 grms. of the ash in each case. The same results were obtained on examining a number of leaves and woods from the Freyburg district. A. L. G.

\* Nobbe's *Landwirthschaftliche Versuchsstationen*, 33, 39-88.

† Report of the Sixth Annual State Viticultural Convention, San Francisco, 1888.

‡ *Pharm. Zeitung*, 83, No. 40, p. 312; *ibid.*, No. 80.

§ *Weinbau u. Weinhandl.*, No. 36, 1888, and ANALYST, Dec., 1888.

# THE ANALYST.

FEBRUARY, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The Annual Meeting of the Society was held on the 9th ult., at Burlington House, Piccadilly, Mr. A. H. Allen in the chair.

The minutes of the previous meeting were read and confirmed.

The auditor's report on the accounts for the past year was read, and will be printed and circulated as usual.

Mr. ALLEN then delivered his valedictory address as follows:—

### THE PRESIDENT'S ADDRESS.

Following the custom which has prevailed in previous years, I now have to bring before you a *résumé* of the past work and present position of the Society.

In the first place, it is gratifying to find that the progress of the Society, so far as it is represented by the number of members, is satisfactory. In addition to the resignation of two associates, three members have been removed from the list for non-payment of arrears of subscription, and six associates for the same reason. To counterbalance this, we have the election of ten new members and four new associates, so that the total number of subscribers is exactly the same as in the previous year; but the number of ordinary members is increased by four, and that of the associates diminished by the same number, the honorary members still numbering ten. The Society has also suffered a loss in the death of Dr. William Wallace, of Glasgow. Dr. Wallace was for many years senior member of the firm of Wallace, Tatlock and Clark, and occupied the post of Public Analyst for Glasgow and several neighbouring counties and boroughs. He ranked as one of the ablest and best-known chemists in Scotland, and although the distance of his residence from London prevented him from regularly attending our meetings, he always took a great interest in the Society. Personally, I feel in the death of Dr. Wallace the loss of an intimate friend, who was always ready to give me the best advice and assistance in his power.



The adulteration of lard has also grown enormously during the past year or two, and, instead of meeting with the large proportions of water formerly so common, lard is now sophisticated in a novel and ingenious manner, namely, by adding a mixture of cotton-seed oil and beef or mutton stearin. Mr. E. W. T. Jones appears to have been the first analyst on whose certificate the prosecution for the presence of cotton-seed oil took place, and he was quickly followed by other analysts. For a time the sale of lard adulterated with cotton-seed oil seems to have received a serious check, but knowing how skilfully such sophistications are conducted, and with the express purpose of baffling the Public Analyst, we may expect that those interested are simply seeking a safe method of eluding our vigilance. For a long time it seemed as if the detection of beef-stearin in lard could only be effected inferentially, and until quite recently I was unable to satisfy myself of the presence of beef-fat in several samples of lard which I strongly suspected to contain it. I believe, however, that difficulty is now surmounted, and with the aid of some hints from Dr. Campbell Brown I have been able to detect positively the presence of beef-fat in lard. The use of cocoa-nut oil as an adulterant of lard does not seem yet to have become very extensive. I have condemned one sample myself on this ground, and have examined another submitted to me from a brother-analyst. But the detection of this adulterant presents no difficulty, and hence the use of cocoa-nut oil is not likely to be very extensively practised.

With respect to butter, the determination of the volatile acids by the Reichert process has of late become fairly general, but I find comparatively few analysts have adopted the precautions found necessary by Professor Wolny, of Kiel, a translation of whose report and paper, by Mr. O. Hehner, was published in the ANALYST last winter. I cannot but feel the gravity of the figures I submitted to the Society at its last meeting, showing that the range of variation in the composition of genuine butter was greater than had been generally recognised; but the fact being absolutely beyond dispute it seemed to me that however much we might regret the immediate consequences of the discovery, it was our plain duty to accept the position, and strive so to modify and improve our methods of analysis as to render it possible to distinguish a butter adulterated with a small percentage of margarine from one which was simply abnormal in composition, and I believe it will be found possible to effect this. A committee has been appointed to investigate the matter. For various reasons, it is not desirable to increase the number of the committee to any great extent, but it is to be earnestly hoped that other Public Analysts, and the members of the Society generally, will co-operate with the committee, who have undertaken work of a very laborious and responsible character. With their help and sympathy much may be done, and it is, in my opinion, a great misfortune that the Public Analysts of this country, who have done so much good work in the past, should have to work under such disadvantageous conditions, and without that encouragement from other chemists which they have a right to expect. That the Government of the country should persistently ignore the Public Analysts as a body, as has been done in his official position by the Chancellor of the Exchequer, among others, is a lamentable fact. The Public Analysts, as a body, are now a set of competent and highly trained men, doing their disagreeable duties without fear or favour, while liable at any time to have their reputations injured by reference to a Court of Appeal, unsatisfactory in its composition, and having a narrow and one-sided idea of its duties.

In a few months the position of some of the Public Analysts will be materially changed, as many will hold their appointments under the newly created County Councils. It is only to be expected that these bodies will, like other new brooms, sweep clean, especially as the only argument for supporting some of the candidates seems to be that they are prepared to reduce salaries all round. Under these circumstances it behoves Public Analysts to stand together and make a determined and united effort to



resist the attempt, which will doubtless be made in some quarters, to reduce still further the already insufficient remuneration of many of those holding appointments under the Sale of Food and Drugs Act.

As to the future, I think we may, at some time, see an amended Act passed. We are sadly in need of a revised system of reference in the case of disputed analyses. Again, it is very desirable that some means should be devised for tracing milk and butter to their sources, so that if peculiarity of composition be really due to natural causes the vendor may have the fact demonstrated, while, on the other hand, it will become more difficult than at present to plead natural poverty of the milk as an excuse.

The Margarine Act has worked fairly well during its twelve months' enforcement, but experience has shown that it is not free from defects which might be very easily removed by an amending Act.

The difficulty of dealing with drugs is, at present, greatly increased from the absence of any authoritative and legal standard, although it is a curious fact that the Pharmacopœia was not made the formal standard in the Sale of Food and Drugs Act Amendment Act, of 1879, simply because Dr. James Bell held that it was *already practically accepted as the standard*. Unsatisfactory as the existing Pharmacopœia is, and discreditable to certain of those entrusted with its compilation, its formal adoption as the legal standard for drugs mentioned therein would be a distinct advantage, and would have the additional good effect of hastening the publication of a new edition, which might be free from the defects which characterise that of 1885.

There are other directions in which the Adulteration Act might be extended and improved. It certainly should apply to such articles as disinfecting powder, which at present escapes through its meshes; and I think it is not too much to hope that in the future we may see its scope extended so as to make it an offence to sell as "all wool" an article which is in great part cotton or other fibre, and even to prevent the false description of articles of jewellery.

And now it simply remains for me to express my regret that I have on many occasions failed to fill this chair in a satisfactory manner. I am fully aware of my own shortcomings in this respect, but have the satisfaction of knowing that in the immediate future the position lately occupied by me will be filled by one in whose care the dignity and interests of the Society of Public Analysts of Great Britain may be left with the fullest confidence.

Mr. ALLEN proposed, and it was unanimously resolved, that a vote of thanks be accorded to the Chemical Society for the use of their rooms during the past year.

The election of Officers and Council for the ensuing year was then proceeded with, and on the ballot-papers being opened it was announced that the following gentlemen were elected:—

*President*.—M. A. Adams, F.R.C.S., F.I.C.

*Vice-Presidents* (who have filled the office of President).—A. H. Allen; A. Dupré, Ph.D., F.R.S.; C. Heisch; Alfred Hill, M.D.; J. Muter, Ph.D., M.A., F.R.S.E. (Who have not filled the office of President).—Sir Chas. Cameron, M.D.; S. Harvey; T. Stevenson, M.D., F.R.C.P.

*Treasurer*.—C. W. Heaton.

*Hon. Secretaries*.—Bernard Dyer, B.Sc.; Otto Hehner.

*Other Members of Council*.—C. E. Cassal; R. H. Davies; W. Fox; R. H. Harland; W. Sedgwick Saunders, M.D.; P. Vieth, Ph.D.; C. R. Alder Wright, D.Sc., F.R.S.

The names of those members of Council whose term of office has not yet expired, and who consequently do not retire this year, are J. Baynes; J. A. R. Newlands; E. Seaton, M.D., F.R.C.P.; W. J. Sykes, M.D.; J. A. Voelcker, Ph.D.

The following gentlemen were also elected :—

As Members : T. S. Gladding, New York ; Professor V. Stein, Copenhagen.

As Associate : Sydney Steel, assistant to Mr. Bernard Dyer.

Mr. ALLEN then vacated the chair, which was thereupon taken by the newly elected President—

Mr. ADAMS, who thanked the members for the honour which had been conferred upon him, and said he was fully conscious of the great gap which their retiring President would leave behind him, but he rejoiced to know that Mr. Allen's large and varied experience would not be lost to the Society—they would have him with them in the future, as they had had, so much to their advantage, in the past. He (Mr. Adams) was, however, afraid that it could not be denied that Mr. Allen had left them in somewhat of a mess—a greasy mess. He had certainly upset the fat in the fire, and they would not want for lack of work in the forthcoming season in clearing up after him. Of course they would have him to assist them, and the wonderful instinct that had put them in the right direction, although he had made this mess just at the end of his term, showed that Mr. Allen was just the one to clear it up for them. In conclusion, Mr. Adams said that he could assure them he should have the greatest pleasure in devoting himself to the interests of the Society, and nothing should be wanting on his part to show how fully he appreciated the honourable position to which they had elected him.

The following papers were read :—

“Remarks on a Recent Case of Alleged Injurious Pollution of the River Medway by the Sewage of Maidstone.” By Dr. Dupré, F.R.S.

The discussion on this paper was adjourned until the February meeting, in the hope that Dr. Tidy and Mr. Wynter Blyth might then be able to attend.

“On the Analysis of Pepper, and the Occurrence of Piperidine therein.” By Dr. W. Johnstone.

“On the Westphal Balance.” By Mr. W. F. K. Stock.

The Annual Dinner was afterwards held at the St. James's Hall Restaurant, where a very enjoyable evening was spent by the members and their friends.

The next meeting of the Society will be held at Burlington House, on Wednesday, the 13th inst., when the adjourned discussion on Dr. Dupré's paper will be resumed.

*(The papers by Dr. Dupré, Dr. Johnstone, and Mr. Stock, will be published in our next issue.)*

## ON THE DETERMINATION OF CITRIC ACID IN LEMON-JUICE.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

*(Read at the Meeting, December, 1888.)*

THE general chemistry of citric acid has already been so ably dealt with in the excellent and exhaustive papers by R. Warrington (*Journal of the Chemical Society*, vol. xxviii., p. 925), and by B. J. Grosjean (*Journal of the Chemical Society*, vol. xliii., p. 331), that it is not necessary for me to dwell at any length on that part of the subject. I may say at once that my special object in bringing this matter before the Society of Public Analysts is to promote a discussion among the members, with the view to attain, if possible, a standard process for estimating the citric acid in lemon-juice, as, in the face of recent improvements in analytical chemistry, this question certainly deserves further

consideration—former methods being more or less unreliable, owing to the unsatisfactory nature of the indicators employed.

Litmus, logwood, and cochineal solutions, all of which have, I believe, been used in the past, are unsuitable indicators, while litmus-paper is, for a reason which will presently appear, not very much better. Samples of lemon-juice are sometimes sent to my laboratory for examination by calico-printers and others, and my results nearly always come out lower than those of Mr. G. H. Ogston, upon whose certificate, lemon-juice is, I understand, generally sold in this country.

These discrepancies having occurred rather frequently, I communicated with Mr. Ogston, in order, if possible, to come to an understanding as to the method to be adopted in the analysis of future samples, so as to avoid any further differences between our results.

In the course of his reply Mr. Ogston said, "The process agreed upon for the commercial analysis of lemon-juice is titration by carbonate of soda solution, using litmus-paper as indicator."

Mr. Ogston then points out certain precautions necessary to be observed, and admits that the exact point at which to cease adding the carbonate of soda is difficult to see, and can be determined only after a good deal of experience.

I was rather surprised to hear of an analyst employing carbonate of soda in estimations of citric acid. I myself use pure caustic soda solution, which I find to be preferable in every respect.

Litmus-paper is also, in my opinion, a very unsatisfactory indicator, as it is affected to a considerable extent by normal citrate of soda—the real end reaction being thus difficult to tell with accuracy.

It is a well-known fact that citrate of soda solution, according to its degree of dilution, turns pink litmus-paper more or less blue, and it becomes, therefore, to a certain extent a matter of chance as to what excess of soda must be added when litmus-paper is used as an indicator.

In order to overcome this difficulty it is, I believe, customary to ascertain the exact strength of the alkali by means of pure citric acid and pale litmus-paper, taking as nearly as possible the same shade of blue for the end reaction, both in standardising and in performing the actual analysis; but even using every precaution, I find this plan to be unsatisfactory, in addition to being very tedious.

In estimating citric acid I have long since discarded litmus as an indicator in favour of phenolphthalein, as recommended by R. T. Thomson (*Journal of the Society of Chemical Industry*, vol. vi., p. 195) and other chemists. This latter indicator I have proved to be quite unaffected by citrate of soda, whereas this salt is distinctly alkaline to litmus, as already mentioned. The end of the reaction is also seen with the greatest precision when phenolphthalein is used, one drop of normal caustic soda solution in excess being sufficient to produce an unmistakable change of colour. No reliance can, of course, be placed on results obtained by titrating with either hydrate or carbonate of sodium in the presence of mineral acids, but in their absence neutralisation with alkali gives a fairly accurate idea of the amount of citric acid present, especially in concentrated lemon-juice.

In the presence of other acids which might interfere with the ordinary soda test it is necessary to employ the calcium chloride process described in Mr. Warington's paper.

The plan which I adopt in the analysis of concentrated lemon-juice is as follows: The specific gravity is first taken at 60° Fah. For this purpose some analysts employ a special hydrometer, termed a "citrometer," on the scale of which every .004 above unity is equivalent to one degree.

As is the case with so many commercial products, the density indication is of little or no value, unless the lemon-juice is free from adulteration. Nevertheless, it is customary to state the "citrometer" indication on commercial certificates. Indeed, many calico-printers in my district actually buy according to the "citrometer" degrees, without paying much attention to the proportion of citric acid present, and thus become ready victims to the wiles of unscrupulous drysalters. In order to determine the total acidity of the juice, I dilute 1,000 grains measure of the sample to 10,000 grains with water in a stopped measuring-flask, and take one-tenth of the whole (equivalent to 100 grains of the original juice) for titration with alkali. This aliquot portion is placed in a large porcelain basin, and diluted with water until the liquid is of a pale yellow shade, and after the addition of a few drops of alcoholic phenolphthalein solution, normal caustic soda solution is run in from a burette until a rose colour appears. In order to avoid any possible chance of error, I always perform the entire process in duplicate. Two determinations of the total acidity should agree within two grains of normal soda solution. The results are calculated into ounces of citric acid per gallon.

As a confirmatory test, another carefully measured portion of the sample may be taken, and without any previous dilution, neutralised with the requisite amount of caustic soda. Rather more than the calculated quantity of a 20 per cent. solution of calcium chloride is next added, and the whole heated in a salt bath for some time.

The calcium citrate is filtered off, washed slightly with boiling water, the filtrate concentrated to a small bulk, taking care to keep the solution neutral, and again filtered. If necessary, the filtrate is again concentrated, and any precipitate which comes down filtered off through a very small filter. The precipitates are gently ignited in a platinum crucible, in order to convert the calcium citrate into calcium carbonate, which is then decomposed by excess of normal hydrochloric acid, filtered and titrated back with normal caustic soda.

When testing genuine samples of lemon-juice I have generally found this process to give figures agreeing fairly well with those obtained by direct titration with soda, the results being in most cases rather lower, owing to part of the total acidity being due to organic acids, other than citric, which do not form an insoluble lime salt.

I have tried the carbonate of soda method used by Mr. Ogston, in comparison with my ordinary process, on several samples of lemon-juice, some of which were taken from pipes imported from abroad, while the others were prepared from lemons pressed and concentrated in my own laboratory. The figures obtained will be found in the accompanying table;—

*Ounces of Citric Acid per Gallon.*

|                            |    |    |    |    |    | NaHO<br>Method. | Na <sub>2</sub> CO <sub>3</sub><br>Method. | CaCl <sub>2</sub><br>Method. |
|----------------------------|----|----|----|----|----|-----------------|--|------------------------------|
| <i>Foreign Samples.</i>    |    |    |    |    |    |                 |  |                              |
| No. 1                      | .. | .. | .. | .. | .. | 68.24           | 69.42                                      | 64.12                        |
| No. 2                      | .. | .. | .. | .. | .. | 63.48           | 64.56                                      | 58.98                        |
| No. 3                      | .. | .. | .. | .. | .. | 61.80           | 62.55                                      | 58.24                        |
| No. 4                      | .. | .. | .. | .. | .. | 62.88           | 63.96                                      | 60.14                        |
| No. 5                      | .. | .. | .. | .. | .. | 60.86           | 61.84                                      | 57.98                        |
| No. 6                      | .. | .. | .. | .. | .. | 66.74           | 67.88                                      | 64.92                        |
| <i>Laboratory Samples.</i> |    |    |    |    |    |                 |  |                              |
| No. 1                      | .. | .. | .. | .. | .. | 94.32           | 94.56                                      | 94.08                        |
| No. 2                      | .. | .. | .. | .. | .. | 63.36           | 64.32                                      | 62.52                        |
| No. 3                      | .. | .. | .. | .. | .. | 75.48           | 76.20                                      | 75.60                        |

These experiments show plainly that titration with carbonate of soda and litmus-paper invariably gives higher results than titration with caustic soda and phenolphthalein. I may say, in passing, that my carbonate of soda results, although so much higher than the caustic soda figures, are lower than those obtained by Mr. Ogston in testing duplicate samples.

*Pure Citric Acid.*—We now come to the consideration of the respective values of normal carbonate and caustic soda solutions, when titrated against pure citric acid, as upon this the value of the process entirely depends. For this purpose I obtained samples of citric acid from seven different manufacturers. Very accurately weighed quantities of each were carefully titrated with pure normal caustic and carbonate of soda, using alcoholic solution of phenolphthalein and litmus-paper as the respective indicators. All the experiments were done in duplicate. In the following table are given the number of grains of the seven samples respectively, neutralised by one hundred grains of normal caustic and carbonate of soda solutions:—

|              |    |    |    |    |    | NaHO. | Na <sub>2</sub> CO <sub>3</sub> . |
|--------------|----|----|----|----|----|-------|-----------------------------------|
| Sample No. 1 | .. | .. | .. | .. | .. | 7.03  | 7.32                              |
| „ No. 2      | .. | .. | .. | .. | .. | 6.96  | 7.37                              |
| „ No. 3      | .. | .. | .. | .. | .. | 6.94  | 7.12                              |
| „ No. 4      | .. | .. | .. | .. | .. | 6.99  | 7.13                              |
| „ No. 5      | .. | .. | .. | .. | .. | 7.09  | 7.26                              |
| „ No. 6      | .. | .. | .. | .. | .. | 7.14  | 7.24                              |
| „ No. 7      | .. | .. | .. | .. | .. | 7.02  | 7.21                              |

On averaging these figures, it will be seen that 100 grains normal caustic soda equal 7.02 grains citric acid, while 100 grains normal carbonate of soda equal 7.23 grains citric acid. For all practical purposes, the 7.02 grains may be regarded as 7 grains, the slight difference being, no doubt, due to the presence of traces of impurities in some of the samples of citric acid. This result would then agree exactly with the figure demanded by theory.

The accuracy of titrations made with caustic soda, using phenolphthalein as in-

indicator, having thus been proved beyond doubt in the case of citric acid, it seems undesirable to employ carbonate of soda in the analysis of lemon-juice, as the estimation then occupies so much longer time, besides not giving such reliable results. I would suggest, therefore, that the citric acid in lemon-juice should in future be determined by titration with caustic soda and phenolphthalein in the absence of interfering bodies, the result to be confirmed, if necessary, by the application of the calcium chloride test previously described.

In conclusion, I should like to add that the calcium chloride method indicated 99.4 per cent. of citric acid, when tried on a portion taken from the mixture of the seven samples of citric acid already referred to.

#### DISCUSSION.

The PRESIDENT said that he was glad to find that Mr. Rowland Williams appreciated the use of phenolphthalein as an indicator. He thought that the tendency was to use phenolphthalein more and more in all cases in which it was suited for the purpose—that is, where a weak acid was to be determined and the absence of carbonic acid could be ensured. He had no doubt that the process of titrating citric acid and lemon-juice by caustic alkali and phenolphthalein was novel so far as Mr. Williams was concerned; but it had been in constant use for some years, to his (the President's) knowledge, in several laboratories where such essays were required, and the process was fully described in his "Commercial Organic Analysis," vol. i. Phenolphthalein always gave very satisfactory results where the colour could be seen; but in the case of very dark juices it sometimes became necessary to have an outside indicator, in which case very delicate litmus-paper, made by brushing a neutral solution of litmus on to white writing-paper, not absorbent paper, was the best substitute for it. Congo-red paper would probably also be valuable. It was disheartening to learn that chemists of repute were still content to titrate lemon-juice with an alkaline carbonate and litmus. He was not surprised that Mr. Williams's results did not agree with those who employed so antiquated and unsatisfactory a process, and there could be no doubt on which side the truth lay. In titrating with phenolphthalein there was one direction in which he thought an improvement might be made, and that was to use a standard solution of baryta instead of caustic soda. Baryta had the advantage that it was certain to be free from carbonic acid, which, of course, was not the case with caustic soda. However, he would have occasion to refer at greater length to this point later in the evening.

Mr. DYER said he happened to know that Mr. Ogston used litmus-paper that was not bibulous, but painted on one side, and that he laid great stress on that.

Mr. WILLIAMS, in reply, said he had not tried congo-red paper, but congo-red solution did not answer the purpose at all.

### THE WERNER-SCHMID METHOD OF DETERMINING FAT IN MILK AND CREAM.

By A. W. STOKES, F.I.C., F.C.S.

(*Read at Meeting December, 1888.*)

Of the various methods of determining fat that I have practically tried, including those of Wanklyn, the Lactobutyrometer, Adams's paper-coil, and the Lactocrite, not one is perfectly satisfactory.

The two former are not accurate, the paper-coil takes too long, and the lactocrite is too expensive and unsuitable for a laboratory.

All who have many samples of milk to analyse will, I think, welcome a method that combines almost the simplicity of the Wanklyn process with the accuracy of the

Adams's paper-coil method, and in addition gives a quickness that neither can pretend to. All this, I believe, the Werner-Schmid method does.

About two months ago, in vol. xxvii., part 4, of the *Zeitschrift für Analytische Chemie*, appeared a notice which was translated into the *Chemical News* of October 19th, 1888, and has since appeared in the December number of the *Journal of the Chemical Society*. It is so short that I quote the whole of it:—

"Dr. Werner-Schmid takes a test-tube of about 50 c.c. capacity, graduated in tenths of a c.c., introduces 5 c.c. of cream or 10 c.c. of milk, accurately measured, adds 10 c.c. of strong hydrochloric acid, boils, with shaking, until the liquid turns dark brown, cools by placing the tube in cold water, adds 30 c.c. of ether, shakes round, lets stand, measures the volume of the ethereal solution, draws off 10 c.c. with a pipette, evaporates down in a weighed porcelain capsule on the water-bath, and finally in an air-bath at 100°. He then weighs and calculates for the original quantity of the ethereal solution. If the process has been rightly conducted, the ether separates from the aqueous solution clear, without the slightest turbidity. The ethereal solution, as it flows out of the pipette, should not show any watery drops. The results are perfectly accurate, and differ from each other and from the ordinary gravimetric methods by less than one-tenth per cent. The operation requires at most fifteen minutes."

Nowhere could I find any further information or any experimental proofs of the accuracy of the method; I therefore now supply my experience. At first I tried to simplify the process by using a 50 c.c. flask, in which it was easier to boil the mixed acid and milk than in a tube. From this, after filling up with ether, I took 10 c.c. for evaporation, assuming that there was present 30 c.c. of ethereal solution of fat. This gave, however, too high results, because some of the ether was taken up by the acid mixture. I now, therefore, use calibrated test-tubes, but do not actually boil the mixture of milk and acid, but plunge the corked tubes into the boiling water of the water-bath for 5 to 10 minutes, then cool them down by immersion in cold water. On adding ether up to the 50 c.c. mark, and vigorously shaking for half a minute, a contraction of the ether takes place; it usually stands at 49·5, while the acid and milk mixture takes up some ether, so as usually to occupy 26 c.c., leaving 23·5 c.c. of ethereal fat solution. After standing for 3 to 5 minutes, this ethereal solution separates completely; 10 c.c. or any aliquot part may be pipetted off and evaporated. I find that flat-bottomed glass dishes, of 2½ in. diameter, are very suitable for rapid evaporation of the portion of ether taken. The whole operation takes from 15 to 20 minutes, but of course a number can be going on at the same time.

*Ordinary milks* gave the following comparative results by the various methods of—

|       | Wanklyn. | Adams. | Schmid. | Calculation. |
|-------|----------|--------|---------|--------------|
| No. 1 | 2·64     | 2·91   | 2·90    | 3·14         |
| No. 2 | 2·53     | 2·71   | 2·70    | 3·11         |
| No. 3 | ..       | 2·48   | 2·37    | 2·95         |
| No. 4 | 2·04     | ..     | 2·53    | 2·70         |
| No. 5 | 2·71     | ..     | 3·08    | ..           |
| No. 6 | ..       | ..     | 2·88    | 3·22         |
| No. 7 | ..       | ..     | 3·48    | 3·61         |

These are a few examples of milks received in the ordinary course from various parishes. Most of them are watered samples, taken from the top of the churn, hence the agreement between the Adams or Schmid with the calculated fat is not so near as usual. It is, however, evident that the Wanklyn process does not extract the whole of the fat, even when, as in some of the cases, the milk after weighing was curdled with acetic acid, and its solids boiled with benzoline for two days. The Adams's process and the Schmid agree, I think, within the limits of experimental error.

*Skimmed milks* gave the following comparative results;—

|        | Wanklyn. | Adams. | Schmid. | Calculation. |
|--------|----------|--------|---------|--------------|
| No. 8  | 0.20     | 0.30   | 0.24    | ..           |
| No. 9  | ..       | 0.51   | 0.50    | ..           |
| No. 10 | ..       | 0.65   | 0.64    | ..           |
| No. 11 | ..       | ..     | 1.14    | 1.24         |
| No. 12 | ..       | ..     | 1.02    | 1.12         |

*Condensed milks*, I find, are best treated by weighing out 10 grms., and diluting this to 100 c.c. with water, then taking 10 c.c. of this for the Schmid process.

A sample gave by Adams's method 12.4, by Schmid's 12.1 per cent. fat.

*Stale milks* are readily treated by this process. When shaking such a milk to obtain a fair sample an enormous mass of gas-bubbles is formed, such as prevent an accurate volume of the milk being taken. If, however, after shaking vigorously, the milk be poured into a 100 c.c. flask, in which 75 c.c. of water are present, with frequent agitation while pouring, all the bubbles will break, and the flask may readily be filled to the 100 c.c. mark. From this four-times-diluted mixture of the stale milk 10 c.c. may be taken for the Schmid process, and be treated as described:—

|        |           |             |          |                               |
|--------|-----------|-------------|----------|-------------------------------|
| No. 13 | gave 3.69 | when fresh, | and 3.63 | after an interval of 39 days. |
| No. 14 | „         | 0.69        | „        | 0.66                          |
| No. 15 | „         | 2.87        | „        | 2.82                          |
| No. 16 | „         | 3.12        | „        | 3.24                          |
| No. 17 | „         | 2.73        | „        | 2.76                          |

*Creams*.—I find it best to weigh out 10 grms. of the sample, and to make this up to 100 c.c. with water, then to take 10 c.c. of the mixture for the Schmid method. Otherwise, if the cream is treated direct, or only slightly diluted, the pipette cannot deliver its proper amount. Besides this, the resulting ethereal solution is so dense as to make it necessary to wait a long time for the other parts of the mixture to settle after shaking. Samples thus treated gave the following results:—

|        | Wanklyn. | Adams. | Schmid. |
|--------|----------|--------|---------|
| No. 18 | 42.8     | ..     | 42.4    |
| No. 19 | ..       | 52.8   | 52.5    |

*The action of the process* is that the acid destroys the casein almost entirely, and acts upon the milk-sugar to produce the brown colour, while the fat is set free and rises to the surface. The ether dissolves this fat, but I think not entirely. There is always a minute amount of fat present in the hydrochloric acid solution. I am trying to find whether this is a constant proportion, so that it might be allowed for.

It is necessary to use ether that has been washed with water, otherwise the alcohol usually present in commercial samples will interfere with the results. No contraction or alteration of volume occurs in the mixture of acid and milk after boiling and cooling, but when the tube is filled to the mark with ether and well shaken a contraction of the total quantity takes place.

I determine the amount of this (usually 0.5 to 1 c.c.) for each tube, and make a mark above the usual 50 c.c. contents-mark, and fill with ether to this before shaking.

The ethereal solution of fat when pipetted off is always acid. I have, however, carefully tested a large number of such combined extracts for milk-sugar, but have never found a trace.

Should the tube, by accident, be filled above its proper mark with ether, it is easy to evaporate off the excess. Should the first portion of ethereal solution be lost, another portion may be readily pipetted off. Doubting whether it was sufficient to shake the mixed fluids for half a minute, and to let stand for 5 minutes only, I have shaken duplicates for longer periods, and have let them stand for 2½ days. The results have been the same. Frequent repetitions of the same milk agree,



It is necessary to see that pipette, burette, and tube are properly graduated and to weigh accurately.

So far the method seems to me to possess the advantages of accuracy, speed, simplicity, cheapness of apparatus, and little loss of reagents. Calibrated tubes, made for the purpose, may be obtained of Messrs. Cetti, Holborn.

### EXAMINATION OF LARD FOR ADULTERATION.

By THOMAS S. GLADDING, NEW YORK.

(Read at Meeting, December, 1888.)

IN the examination of lard the following tests have been found most reliable:—

(1) Specific gravity at 100° C. (2) Hübl's Iodine test. (3) Milliau's modification of Bechi's test. (4) Dalican's "Titre" test. (5) Belden's microscopic test for beef fat, as described by Professor Sharples in a late number of the ANALYST. No lard should ever be condemned by a single test. A certificate should never be given except one based upon a full examination.

The "titre" is Dalican's crystallising points of the fatty acids. The term is a very convenient abbreviation, and the value of the test itself will appear from the results of the work done.

The following table gives the tests of eight samples of whose purity no doubt is entertained. Samples 4, 5, 7 were tried in our laboratory. Samples 1, 2, 6, 8 were received from reliable houses, and their purity guaranteed. Most of the work was done in careful duplicate. Hübl's method was strictly followed, the hyposulphate solution being standardised by chemically pure iodine prepared by ourselves, and also by chemically pure iron ammonia sulphate.

|                                   | Specific Gravity<br>at 100° C. | "Titre."<br>31·40° C. | Iodine Test.    |
|-----------------------------------|--------------------------------|-----------------------|-----------------|
| 1. Lard oil ... ..                | —                              | 31·40° C.             | 74·60 per cent. |
| 2. Lard (very soft) ... ..        | 0·8610                         | 36·40                 | 68·40           |
| 3. Lard ... ..                    | 0·8614                         | 36·40                 | 67·60           |
| 4. Leaf lard, 1 (soft) ... ..     | 0·8610                         | 38·20                 | 65·80           |
| 5. Leaf lard, 2 (hard) ... ..     | —                              | 41·40                 | 57·00           |
| 6. Lard stearine ... ..           | —                              | 43·50                 | 49·50           |
| 7. Beef fat (soft yellow) ... ..  | —                              | 41·60                 | 43·80           |
| 8. Cotton-seed oil (summer white) | 0·8690                         | 33·30                 | 108·00          |

The striking point in the above table is the wide range of the iodine test on samples of lard of undoubted purity. The highest tests hitherto published have been about 61 to 62 per cent. With soft lards the figures 67·60 and 68·40 were obtained. The above "titre" tests at once explain this great range of the iodine tests. From Dalican's table we find that a tallow having a titre of 41·40° C. contains approximately 59 per cent. of olein, and one of 43·50 contains 53 per cent. of olein. The iodine absorbed will vary approximately with these varying proportions of olein. In any examination, therefore, of lard the titre of the sample should be known, in order to interpret the meaning of the iodine test. The wide difference between the titre 31·40 of lard oil and 43·50 of lard stearin and the corresponding iodine tests of 74·60 and 49·40 is a further and more extreme illustration of the same truth. The beef fat in the table was a soft yellow fat of lower titre than usual. The common titre of prime solid beef fat is about 44, and would show an iodine test of about 40, the number usually given for beef. Comparing the iodine test 43·80 of beef fat above with the iodine test of 56·20 of lard of about the same titre, it becomes apparent that there is some difference in the chemical nature of the two fats which is demonstrated by the iodine test, but not revealed by the

titre. I have been informed by good authority that the cotton-seed oil (summer white) in the above table is the form commonly used for adulteration of lard, and not the cotton-seed stearin as has been stated. The low titre of 33.30 is therefore interesting, and its influence will appear in some analyses to be given later. I have made thorough trial of Belden's microscopic test, and have been greatly pleased with it. It is very valuable for the detection of beef fat in lard, and in most cases is the ONLY reliable test for that adulterant, but requires much practice with samples of known purity and samples of known percentage of adulteration.

The following analyses of samples sent in for examination will prove interesting. Four samples were sent in to determine the chemist's ability to detect adulteration. One sample was to be pure lard, another adulterated, and the other two were to be the products of rival houses that were suspected of adulterating their goods. The samples were numbered 1 to 4, with no other mark.

|                             | 1         | 2          | 3                 | 4                 |
|-----------------------------|-----------|------------|-------------------|-------------------|
| Specific gravity at 100° C. | 0.8610    | 0.8606     | 0.8636            | 0.8631            |
| Titre .. ..                 | 36.40     | 39.60      | 36.15             | 36.60             |
| Iodine test .. ..           | 68.40     | 58.33      | 76.60             | 75.40             |
| Belden test .. ..           | Lard.     | Beef lard. | Beef lard.        | Beef lard.        |
| Bechi-Milliau test ..       | Negative. | Negative.  | Strong darkening. | Strong darkening. |

Nos. 3 and 4 are at once seen to contain cotton-seed oil from sp. gr., from iodine test, and from Bechi-Milliau test. Sample 2 would be called pure lard, but the crystals of beef fat were formed so readily and abundantly as to show at least 20 per cent. of that adulterant. The impossibility of detecting beef fat without Belden's test is at once evident.

The very low titres of 3 and 4 need explanation. These samples contain at least 25 per cent. of beef fat. The titre should, therefore, be at least 38. The explanation is found in the presence of cotton-seed oil, similar to that in the table, having a low titre of about 33, by which the titre of the mixture is correspondingly lowered. The approximate percentages of cotton-seed oil can only be deduced from specific gravity. Taking that of normal average lard as 0.861, and that of cotton-seed oil as 0.869, we conclude there must be about 32.5 per cent. and 26 per cent. of cotton-seed oil respectively in these two samples.

Two other suspected samples have just given the following results:—

|                               | 1              | 2              |
|-------------------------------|----------------|----------------|
| Specific gravity at 100° C... | 0.8600         | 0.8606         |
| Titre .. ..                   | 38.00          | 38.80          |
| Iodine test .. ..             | 65.40          | 60.27          |
| Bechi-Milliau test .. ..      | Blackening.    | Negative.      |
| Belden test .. ..             | Much beef fat. | Much beef fat. |

Judged by special gravity and by iodine test, both samples would be pronounced pure. The Bechi-Milliau test in sample No. 1 finds marked confirmation in the fact that though at least 20 per cent. beef fat is present, yet the iodine test, instead of dropping to at least 60, as we should expect from the reducing action of the beef, remains as high as is ever found in a pure lard showing a titre of 38° C. The presence of 5 to 10 per cent. cotton-seed oil can be positively affirmed in view of the whole analysis. Ten per cent. of cotton-seed oil might not have any visible effect on specific gravity, but would raise the iodine test from 65.4 to 70, which in turn is reduced in the above sample to 65.40 by the presence of, say, 20 per cent. of beef fat.

The fatty acids are prepared by saponifying in such a way as to secure as colourless fat acids as possible. They are washed in a separating bulb with several additions of

very hot water, and finally filtered through a dry filter paper into a test tube of  $1\frac{1}{2}$  to 2 centimetres diameter. The "titre" is taken with a delicate thermometer graduated to tenths of a degree. 5 c.c. are then tested for cotton-seed oil by Bechi-Milliau test, and the remainder may be used to ascertain the combining number. A portion also can be used to obtain the iodine number. The iodine absorbed by the fat acids, multiplied by 25.5 (in the case of fats consisting of stearin, palmitin, and olein), will give the iodine absorbed by the original oil.

The great advantage of Dalican's method over any other method of finding the melting-points of oils is the accuracy of the results obtained. The results are correct, as proved by scores of duplicate tests to within .1, or at most .2 degrees Centigrade.

While the above work seems to destroy the value of Hübl's iodine test for examining lard (by itself), yet it by no means cripples the analyst in his ability to reach a correct conclusion when the examination is made a complete one, and all the data attainable have been ascertained.

## ON THE ACTION OF IRON PIPES (RUSTED) UPON WATER CONVEYED THEREIN.

By S. HARVEY, F.C.S., F.I.C.

*Read at Meeting, December, 1888.*

That iron-oxide effects some changes upon certain constituents of drinking water, specially as regards the nitrates present, has long been known, and I lay claim to no originality in bringing the following observations before the Society of Public Analysts.

Nine months ago (March) the Public Water-supply of the Borough of Ramsgate was extended to the village of Minster, the latter place having previously derived its water for drinking purposes from private wells, most of which were polluted.

No sooner however had the Ramsgate supply reached Minster than complaints were made as to its character and appearance. It was very turbid, depositing ferruginous sediment, and when submitted to analysis was found to yield in addition to a considerable amount of combined chlorine "high figures" for "*Ammonia*," "*Oxygen absorbed*," and "*Nitrites*," and this state of things has now continued for several months.

Samples taken from the new supply at Minster were submitted to me, and I had some difficulty in convincing the senders that the appearance of the water was not due to sewage or organic impurity.

As my acquaintance with the Ramsgate water has extended over several years, and as the supply is very pure and uniform, ranking among first-class waters, I felt that a good opportunity presented itself for testing the action of iron pipes (presumably rusted) upon water of a known constant composition. Accordingly I had a number of samples taken all at one date, July 23rd last, and with as little interval between each as the distance would allow. Every care was used both in the collection of the samples and the analysis, which followed immediately. In the case of the *turbid* samples the clear supernatant water only was analysed.

None of these samples contained sufficient iron in *solution* to affect "*ammonium sulphide solution*."

Samples 1, 2, and 3 were taken from the old Ramsgate mains, Samples 4, 5, and

6 were taken at Minster after a run of from five to six miles through the new mains to the latter place, the pipes being four, five, and six inches in diameter.

## PUBLIC WATER SUPPLY, RAMSGATE.

|   | Taken at Ramsgate (old mains). |             |        | Taken at Minster (new mains). |             |             |
|---|--------------------------------|-------------|--------|-------------------------------|-------------|-------------|
|   | No. 1                          | No. 2       | No. 3  | No. 4                         | No. 5       | No. 6       |
| Appearance  | clear                          | clear       | clear  | clear                         | very turbid | turbid      |
| Combined Chlorine   | 5·60                           | 5·60        | 5·25   | 5·53                          | 5·88        | 5·60        |
| Nitrogen as Nitrates<br>and Nitrites                          | 0·72                           | 0·74        | 0·72   | 0·19                          | 0·49        | 0·58        |
| Ammonia   | trace                          | trace       | trace  | 0·0182                        | 0·0168      | 0·0025      |
| Albuminoid NH <sub>3</sub>                                    | 0·0017                         | 0·0017      | 0·0018 | 0·0016                        | 0·0014      | 0·0022      |
| Oxygen in 4 hours   | ·024                           | ·024        | ·028   | ·090                          | ·118        | ·068        |
| Total Solids  | 35·70                          | 35·63       | 36·19  | 29·89                         | 34·79       | 34·72       |
| Deposit   | very slight                    | very slight | slight | slight                        | Iron-oxide  | Iron-oxide  |
| Nitrites  | none                           | none        | none   | in quantity                   | in quantity | in quantity |
| Total Nitrogen in<br>NH <sub>3</sub> Nitrates and<br>Nitrites | 0·720                          | 0·740       | 0·720  | 0·205                         | 0·504       | 0·582       |
| Nitrogen Missing  | —                              | —           | —      | 0·522                         | 0·223       | 0·145       |

N.B.—The figure for combined chlorine in the Ramsgate water fluctuates a little, and differs but little from what it was five years ago.

Omitting details common to both sets of samples, it will be observed that the nitrates have diminished considerably in the last set (4, 5, and 6). The ammonia has risen from traces in the first set to considerable amount in the latter, while nitrites appear in quantity in the latter, their amount being measured *practically* (minus a small deduction) by the oxygen absorbed.

Two questions present themselves. What has become of the missing nitrogen in the three last samples, and how may the small but distinct variations of combined chlorine be accounted for?

There is also a moral consequent upon the above, which was the chief reason for my bringing this matter before the Society.

How far is an analyst justified in pronouncing an opinion upon the purity of a drinking water in the absence of *all* information as regards the *origin* and mode of storage and conveyance of the same, or when such particulars are purposely withheld?

It would be interesting to know how the Minster supply would fare in the hands of an analyst who had been kept in ignorance of its antecedents.

In connection with this subject, viz., the effects of iron oxide upon water, perhaps the following analyses may be interesting, and they confirm some remarks by Dr. E. Frankland (*vide Water Analysis* p. 19).

The water from these wells has been a cause of unpleasantness between analysts in my own experience, very pure as it is.

WATER FROM "LOWER TERTIARIES," (THANET BEDS) BELOW "LONDON CLAY."  
Taken from wells six miles N.N.W. of Canterbury.

|                                    | No. 1                | No. 2               |
|------------------------------------|----------------------|---------------------|
| Appearance .. .. .                 | very turbid          | rather turbid       |
| Combined Chlorine .. .. .          | 7·14                 | 7·14                |
| Phosphates .. .. .                 | very distinct traces | distinct traces     |
| Nitrogen as Nitrates .. .. .       | 0·02                 | 0·02                |
| Ammonia .. .. .                    | 0·1190*              | 0·0878*             |
| Albuminoid Ammonia .. .. .         | 0·0014               | 0·0019              |
| Oxygen absorbed in 4 hours .. .. . | ·023                 | 0·026               |
| Total Solids .. .. .               | 52·78                | 52·22               |
| Deposit .. .. .                    | chiefly Ferruginous  | chiefly Ferruginous |
| Sulphates .. .. .                  | present              | present             |
| Nitrites .. .. .                   | absent               | absent              |

Canterbury, December 10, 1888.

(Conclusion of the Society's Proceedings.)

### NATURAL APERIENT BITTER WATERS.

BY OTTO HEHNER.

SOME time ago the attention of the medical profession was drawn to the important subject of accuracy in dispensing of medicines, by the publication of a joint report by Dr. Edward Seaton and myself. That report having been productive of some good, I venture now to refer to an allied subject, in the hope that a remedy may be found for an evil which concerns medical men and the public alike.

For a number of years past the sale of natural aperient magnesian waters has been considerably increasing, and there is now a large variety of such waters at the disposal of the practitioner. These waters are generally sold in bottles, upon the labels of which, in most cases, analytical figures are printed, which allege to represent the composition of the contents, and are doubtless intended as a guide in fixing the dose of the water to be used. There are also, generally, directions on the bottles to the effect that a wineglassful is the average dose.

It should be generally known that the waters in question, being obtained in the majority of cases from very shallow wells, are liable to very wide fluctuations in composition and consequently in therapeutical activity, and that it is impossible to represent, once for all, the composition of the waters by a single analysis. True mineral waters, coming from great depths, may and do remain unchanged in composition for a long number of years, but magnesian bitter waters, as at present collected, fluctuate in strength almost from day to day; stronger waters collect at the bottom of the wells than in the upper strata, and it is possible, therefore, to obtain at will strongly or relatively slightly saline solutions from the same well.

The following analyses, obtained from samples which I have lately purchased in the London market, represent six different waters, all coming from the Ofen district in Hungary, and frequently taken to be equivalent of each other.

10,000 parts contained:—

|                    | A      | B      | C      | D      | E      | F      | G      |
|--------------------|--------|--------|--------|--------|--------|--------|--------|
| Sulphuric acid..   | 187·56 | 197·08 | 232·20 | 242·34 | 247·48 | 279·37 | 310·60 |
| Chlorine ..        | 13·80  | 15·95  | 8·87   | 10·60  | 10·30  | 13·85  | 14·00  |
| Carbonic acid ..   | 2·29   | 2·51   | 3·87   | 4·36   | 3·08   | 5·81   | 5·06   |
| Magnesia ..        | 54·00  | 53·19  | 56·85  | 71·95  | 65·66  | 97·24  | 101·60 |
| Lime ..            | 6·52   | 6·12   | 6·36   | 6·42   | 6·24   | 7·22   | 7·27   |
| Soda ..            | 67·75  | 79·36  | 91·74  | 87·88  | 96·40  | 91·05  | 92·17  |
| Specific gravity.. | 1031·1 | 1032·7 | 1037·0 | 1039·5 | 1039·7 | 1048·7 | 1049·6 |

Samples D and G represent the same brand of water at different times.

To render these analyses more readily comparable with each other, I will assume that the whole of the magnesia and soda is present in the form of sulphates, which may the more readily be done as the proportions of carbonate of magnesia and chloride of sodium are small, and but little different in the seven samples :—

|                    |          |        |        |        |        |        |        |
|--------------------|----------|--------|--------|--------|--------|--------|--------|
| Magnesium sulphate | ..162·00 | 159·57 | 170·55 | 215·85 | 196·98 | 291·72 | 304·80 |
| Sodium sulphate    | ..155·16 | 181·76 | 210·11 | 201·27 | 220·79 | 208·53 | 211·09 |
|                    | 317·16   | 341·33 | 380·66 | 417·12 | 417·77 | 500·25 | 515·89 |

Taking the proportion of magnesium sulphate as the standard of strength, it is seen that of sample B 1·91 parts are necessary to produce the same effect as one part of sample G.

As the laxative powers of magnesium sulphate and sodium sulphate are nearly equal, we may more fairly compare the totals of the two salts as the measure of the activity of the waters. In that case, 1·63 parts of sample A are equal in effect to one part of G.

The readiest measure of the strength is the specific gravity. According to this A stands to G as 1 to 1·59, the quantities to be taken being of course inversely proportional.

It appears to me that the medical profession should be distinctly aware of the wide differences in the composition of these waters, and should either insist upon some measure of uniformity, which by care in bottling the waters could easily be obtained, or upon an exact statement of strength upon each bottle, be it by analytical figures, or by specific gravity only.

Imagine a patient who has been accustomed to a particular dose of, say, water A, taking an equal dose of sample G. The purgative action would be increased by almost two-thirds. Even if serious consequences might not be the result, the uncertainty of the remedy is apparent.

There could not be any practical difficulty whatever to obtain uniformity in composition, by excluding from the wells all surface water, or such coming from strata poor in saline ingredients. Even then fluctuations, but within narrower limits, would occur. An exact statement of the specific gravity of the contents of each bottle should therefore be made, so that any medical man would be in a position exactly to determine the necessary dose.\* The analyses at present given upon the labels are of no value whatever for this purpose, as they do not represent the composition of the contents, but of samples specially selected to show high saline proportions, and often made many years ago.

### A NEW PEPPER ADULTERANT.

By F. WALLIS STODDART, PUBLIC ANALYST FOR BRISTOL.

A new material in extensive use for the adulteration of pepper having recently come under my notice, I wish to call the attention of public analysts to it, that a united effort in all quarters may stamp out what bids fair to become a very successful fraud.

The material in question consists of rice starch, barytes, calcic carbonate, and lead chromate, all, of course, finely ground and intimately mixed. The lead chromate amounts to about 10 per cent. of the whole compound. By the addition of about 5 per cent. of this mixture, the colour of pepper is so immensely improved as to raise

\* The figures of the specific gravity above 1,000 very nearly representing the sum of the magnesium and sodium sulphates per 1,000 parts of the water. Thus in sample A a specific gravity of 1031·1 corresponds to 31·7 parts of the sulphates per 1,000 of the water.

its market value very considerably, but I have met with pepper containing fully 10 per cent.

Such confidence do the manufacturers of this delectable mixture feel in it, that they guarantee their peppers coloured with it to be genuine, and I saw one invoice endorsed, "warranted genuine as per Somerset House analysis."

Nevertheless the detection of this adulteration is not difficult. The increased ash and presence of rice would arrest attention, whilst the peculiar and unnatural tinge communicated by the chromate is readily noticeable. The method of examination, however, which has proved most successful in my hands is agitation with chloroform, by which means the mineral ingredients of the adulterant are obtained in their natural combinations.

The well-washed residue is gently warmed until the chloroform has evaporated, treated with a very little sodic carbonate solution and allowed to cool. A few drops of ether, which has been agitated with aqueous hydrogen peroxide, are then added, and the mixture carefully acidified with hydrochloric acid, when the delicate blue colouration is readily obtained, and the barium and lead remain to be estimated in the usual way.

## MONTHLY RECORD OF GENERAL RESEARCHES INTO ANALYTICAL CHEMISTRY.

ESTIMATION OF STARCH FOR TECHNICAL PURPOSES. H. SCHREIB. *Zeitschr. f. angew. Chemie*, No. 24, 1888.—The author recommends to estimate the proteids by combustion, and also to take the moisture and the ash. The starch is thus found by difference, but an allowance is made for other carbo-hydrates and fatty matter. Although it seems at first sight absurd to make three determinations instead of one, in practice this way will be found more convenient than a direct estimation of the starch. The best direct process as yet known, viz., Lintner's, takes more than 6 hours, in which time it is much easier to finish the combustion and do the water and ash. Even if Lintner's process left nothing to be desired from a point of accuracy, it will still give unreliable results to the starch manufacturer, because no notice is taken of the starch, which will be retained by the albuminous matter. The author finds that every pound of gluten will cause the loss of one pound of starch. Soluble proteids will, of course, cause no loss. The value of a commercial starch is best got at by direct experiment. Four parts of starch boiled with fifty parts of water must give a proper set paste. Before boiling the starch must be powdered and thoroughly mixed with the water. L. DE K.

IMPURE REAGENTS. L. L. DE KONINCK. *Zeitschr. f. angew. Chemie*, No. 1, 1889.—Lead peroxide often contains manganic peroxide. Being sometimes used for the detection of traces of manganese, it is important to know whether it is perfectly free from that body. Mere boiling with nitric acid will not be always successful. The best way is to first heat a portion of the powder with strong sulphuric acid to dryness, which will yield plumbic and manganous sulphates. A fresh quantity of the lead is now added and the whole boiled with nitric acid, when the test will be successful. Ether often deserves the name of *sulphuric ether*, as it sometimes actually contains free sulphur. This impurity will be easily detected by shaking the sample with mercury, which will more or less blacken. Chloroform often contains alcohol. The usual test is agitation with alkaline permanganate, which should not turn green. The author found this test not to be reliable, as the greening may be caused by impurities in the potash. He therefore uses a solution of potassic permanganate in baryta-water. L. DE K.

## MONTHLY RECORD OF ANALYTICAL RESEARCHES INTO DRUGS.

"IMPERIALIN," A NEW ALKALOID. K. FRAGNER. *Berichte*, Dec. 12, 1888.—The author examined the bulbs of the poisonous crown imperial, *fritillaria* or *coronaria imperialis*, of the family *liliaceae*, and prepared a new alkaloid, "imperialin," by two processes, of which the following is the best: The crushed bulbs are rubbed up with lime, and the mixture completely dried on the water-bath, and repeatedly extracted with hot chloroform, which is afterwards shaken up with water containing tartaric acid. The concentrated acid solution is precipitated with  $\text{Na}_2\text{CO}_3$ , and the precipitate freed from mother-liquor by means of the suction-pump. By repeated re-crystallisation from alcohol, the substance is obtained perfectly white. The yield is about 0·08 to 0·12 per cent. The formula Fragner calculates from his combustions (the carbon determinations vary considerably) is  $\text{C}_{33}\text{H}_{60}\text{NO}_4$ . The alkaloid gets yellow at  $240^\circ$ , brown at  $248^\circ$ , and melts completely at  $254^\circ$ . It crystallizes in short, colourless needles, is very slightly soluble in water, soluble in alcohol—especially so on warming—less soluble in ether, benzene, petroleum-ether and amyl-alcohol, dissolving very readily in chloroform. Its solutions have a bitter taste. Imperialin turns the plane of polarised light to the left. Fragner gives the specific rotation  $[\alpha]_D^{25} = -35\cdot40^\circ$ . Tannin precipitates the solutions of imperialin salts yellow, flocculent; potassium iodide, dark yellow, amorphous; potassio-mercuric iodide, reddish-yellow, flocculent; potassium bismuth iodide, orange-red; potassium cadmium iodide, white flocculent; potassium bichromate, yellow, crystalline; picric acid, yellow, flocculent. The following reactions of the dry substance are given. With concentrated  $\text{H}_2\text{SO}_4$ , a yellow colouration; mixed with sugar and then treated with  $\text{H}_2\text{SO}_4$ , the colouration is first yellowish-green, then pale-brown, flesh-coloured, cherry-red, and finally dirty-violet. Fröhde's reagent becomes greenish-yellow with it, Mandelin's, olive-green, reddish-brown, and finally dark brown. After trituration with cold  $\text{H}_2\text{SO}_4$ ,  $\text{KNO}_3$  and  $\text{KClO}_3$  give orange-yellow colourations, which become dark reddish-yellow if the acid solution has previously been warmed. Warm  $\text{HNO}_3$  colours the alkaloid yellow. With  $\text{HCl}$  a strong fluorescence is produced; on warming, a brownish-green colouration is obtained, which gradually turns brownish-red. No pressure is observed on opening tubes in which imperialin and  $\text{HCl}$  have been heated to high temperatures; therefore, no easily-removable methyl-groups are in the compound. Preliminary experiments seem to show that imperialin acts on the heart. A. L. G.

## LAW NOTES.

ADULTERATED CHEESE.—At Glasgow Sheriff Court, on the 28th December, Sheriff Guthrie presiding, Alexander Moffat, 36, Orr Street, was charged, at the instance of Mr. Peter Pyfe, sanitary inspector, with having on Thursday, 27th September, sold 1 lb. of cheese which was not of the nature, substance, or quality demanded by the purchaser, in respect that it contained 14·12 per cent. of fat which was not butter fat. He pleaded not guilty, and was defended by Mr. T. C. Young and Mr. John A. Spens. Mr. R. G. Ross appeared for the prosecutor.

Mr. Spens objected to the relevancy of the complaint, on the ground that there was no averment that a little added fat took away from the character of the cheese.

The Sheriff repelled the objection on the merits, but said that the points might be raised as the case went on.

Dr. Tatlock, who analysed the cheese, reported that it contained 37·46 per cent. of casein, 12·56 of butter fat, 14·12 of foreign fat, 3·94 of mineral matter, and 31·92 of water.

\* Cross-examined by Mr. Spens: The proportion of butter fat in a skim-milk cheese ranges from 1 per cent. to 10 per cent. So far as he could judge, there was a greater proportion of butter fat in the cheese analysed than in the ordinary skim-milk cheese. A cheese made purely from sweet milk would contain about 33 per cent. of fat. That fat would be all butter fat. He detected the presence of foreign fat by the absence of butyric acid. That was the best method of testing. Butyric acid is always present in butter. There was, of course, some butyric acid in the cheese in question, but there was certainly not so much as there ought to be. He believed the foreign fat in the cheese was quite wholesome, and he believed the cheese was quite wholesome and nutritious. Personally, he would as soon eat these cheeses as skim-milk cheese. There was more fat in them than in skim-milk cheese, but less of the other nourishing ingredients. The foreign fat could not be got in without taking out some of the other nourishing ingredients, such as casein. The percentage of casein in skim-milk



cheese ranges from 35 to 45 per cent. In this particular case he found 37.46 per cent. of casein. The percentage of water should be 25 to 35 per cent., and of mineral matter from 3 to 6 per cent. Nourishment is got from the fat, but he would not call it the principal source of nourishment, for there is also casein. There was cheese made in America mixed with fat. It was sent here in large quantities, and sold as cheese, but he did not allow that it was cheese.

By Mr. Ross: He believed the latter class of cheese was called *margarine* cheese in America. Skim-milk cheeses made in this country are very dry. The addition of foreign fat gave the cheese an appearance of being richer—more like a sweet-milk cheese.

This closed the case for the prosecution.

Preceptor Alexander Osborne was the first witness called for the defence. He stated that he is a partner of the firm of Alexander Osborne and Sons, cheese merchants, Candleriggs, and a shareholder in the Creamery Company, Dunragit, who made the cheese in question. What was formerly known as skim-milk cheese is almost an unsaleable article now. It is of very poor quality, and to make a saleable article they found it necessary to improve it by adding a little fat, which made it rather dearer than skim-milk cheese. This is about the cheapest quality of cheese sold in the market. The retail price of the lowest quality of sweet-milk cheese at present ranges from 6d. to 10d. Sweet-milk cheeses are commonly understood to be made from milk that is not skimmed, but cheeses that are made from milk as it comes from the cow are properly called whole-milk cheeses. No one could expect to get whole-milk cheeses at 4d. per lb. The price indicated that they were something different from what were sold as sweet-milk cheese. The cheeses in question were superior to skim milk cheeses, because fat was added that made them soft and more digestible. The added fat compensated for the cream that was taken away, and made the cheese very nearly, if not quite, as good as the dearer article sold as sweet-milk cheese, and much better than some of them. Originally all Scotch cheeses were skim-milk cheeses, but when the system was changed in the parish of Dunlop the cheeses made there from whole milk were called Dunlop cheeses, to distinguish them from what were called Scotch cheeses.

By Mr. Ross: No person tasting the cheeses in question would distinguish them from ordinary cheeses, except that they might be rather better. Dunragit cheeses have been in the market for two or three years, and the company would prefer that shopkeepers should sell them by that name. Cheeses mixed with foreign fat have been made elsewhere for a long time, but not in Scotland, so far as he was aware.

Mr. Andrew Clement gave similar evidence. The fat introduced into the cheese is cow fat, pure and wholesome.

The Sheriff remarked that if there had been an attempt to sell the cheese at 6d. the case would have been different, but it was sold at 4d., which was not a price above its value.

Mr. Ross contended that when a purchaser asked for cheese he was entitled to get cheese that was made entirely from milk.

The Sheriff said he was satisfied that the case fell under the proviso in the 6th section of the Food and Drugs Act, "Where any matter or ingredient not injurious to health has been added to a food or drug because the same is required for the production or preparation thereof as an article of commerce in a state fit for carriage or consumption." That must be read as meaning that it was intended to prepare the article for consumption with reference to the price that was to be paid for it and the purpose for which it was intended. It was quite clear that there was not in this case anything done "fraudulently to increase the bulk, weight, or measure of the food or drug, or conceal the inferior quality thereof." What the result of another prosecution for a similar case might be it would be wrong for him to prognosticate, but from the evidence it was clear that this case did not fall within the section. The case was accordingly dismissed.

In his report, which was included in the minutes of the Health Committee, Mr. Peter Fyfe, sanitary inspector, in referring to the above case, says that, in giving decision in favour of the accused, his lordship said that the sixth section of the Adulteration of Food and Drugs Acts must be read as meaning "that it was intended to prepare the article for consumption with reference to the price that was to be paid for it and the purpose for which it was intended." It was quite clear that there was not in this case anything done "fraudulently to increase the bulk, weight, or measure of the food or drug, or conceal the inferior quality thereof." The principle here laid down that "foreign" fat may be introduced legally into cheese, so long as the fat used is not injurious, and the cheese is sold at a moderate price, is (says Mr. Fyfe) a new one, which places cheese in the list of *manufactured* articles, and displaces it as a purely milk product. This lays the market open to large importations of "imitation cheese" from America.

Mr. Crawford said he did not desire to say very much about the case. The Committee were not satisfied with the decision, and they had the matter fully under view, and would in course of time take such measures as seemed to them necessary in the circumstances.

#### APPOINTMENTS.

Dr. H. Leffmann has been appointed Pathological Chemist to the Jefferson Medical College Hospital, Philadelphia.

Mr. Beam has been appointed Demonstrator of Chemistry at the Pennsylvania College of Surgery.

# THE ANALYST.

MARCH, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

AN ordinary meeting was held at Burlington House, on Wednesday, the 13th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

The adjourned discussion on Dr. Dupré's paper on "A Recent Case of Alleged Injurious Pollution of the River Medway by the Sewage of Maidstone," was then resumed and concluded.

The following papers were subsequently read and discussed :—

"On the Composition of Milk and Milk Products." By Dr. Vieth.

"An Improved Method for the Analysis of Fats." By Dr. J. Muter and L. de Koningh.

"Note on Phytosterin." By Otto Hehner.

"On Density." By H. Droop Richmond.

The next meeting of the Society will be held at Burlington House, on Wednesday, the 13th inst., at 8 o'clock.

## PEPPER ANALYSIS AND THE OCCURRENCE OF PIPERIDINE THEREIN.

BY WILLIAM JOHNSTONE, PH.D., F.I.C., F.C.S., ETC.

(Read at Meeting, January, 1889.)

MR. PRESIDENT AND GENTLEMEN,

The subject of the paper I have the honour of reading before you this evening is "Pepper Analysis and the Occurrence of Piperidine therein."

What is known as black pepper is the dried immaturred fruit of *Piper Nigrum*, belonging to the *Natural Order Piperaceæ*.

The shrub or plant is a native of tropical regions, and is cultivated in various parts of the Indian Archipelago and in the West Indies, and that imported into this country comes principally from the Islands of Malacca, Java, Borneo, and Sumatra.

The plants of the order of Piperaceæ contain an acid resin, a volatile oil, a volatile alkaloid, and a crystalline substance called piperine. They possess pungent aromatic, astringent, and narcotic properties.

*Botany.* Perennial, *Stem*.—Its stem is 8 to 12 ft. long, trailing or climbing, shrubby, flexuose, and dichotomously branched, jointed, swelling at the joints and often throwing out radicles there, which adhere to bodies like the roots of ivy, or become roots, striking into the ground.

*Leaves*.—From 4 to 5 in. long, alternate, distichous, broadly ovate, acuminate, of a full green and glossy colour, paler beneath, five to seven-nerved, the nerves connected by lesser transverse ones or veins, and prominent beneath.

*Inflorescence*.—Spikes opposite the leaves, chiefly near the upper ends of the branches; shortly stalked, pendulous, 3 to 6 in. long; petioles rounded, from  $\frac{1}{2}$  to nearly 1 in. long.

Flowers unisexual or hermaphrodite, small, whitish.

*Fruit*.—Distinct, braccate, ripening irregularly all the year round, about the size of a pea, at first green, then red, afterwards black, covered with pulp.

The black pepper of commerce consists of the entire berries, with the pulp adhering, gathered before they are quite ripe and dried in the sun. The commercial varieties are at least ten in number, viz., Acheen, Alleppy, Kampoot, Lampong, Penang, Siam, Singapore, Tellicherry, Trang, and Long pepper, the names indicating the localities from whence they are obtained.

Blyth remarks that "the differences which these different varieties of pepper present to the eye are evident enough when the several samples are at hand for comparison," a statement I by no means agree with, "but it takes a very practised observer to identify a solitary sample; and if samples of each of the kinds were mixed together, it is doubtful whether an adept even could separate the berries again, identifying each sort with any correctness." Very doubtful, I should say, indeed.

The merchant, however, relies more upon the weight than the appearance. Taking a handful of peppercorns, he can tell in a moment whether it is a light or a heavy sample, and thereby judges the quality of the pepper.

That there is a difference in the weight of the various varieties of the different peppercorns is evident from the results obtained by the author, who carefully three times weighed 100 berries of each kind, which gave the following average results:—

Average of Three Weighings of 100 Peppercorns.

|               |    |    |    |        |       |
|---------------|----|----|----|--------|-------|
| Acheen        | .. | .. | .. | 5.1976 | grms. |
| Alleppy       | .. | .. | .. | 3.8438 | "     |
| Kampoot       | .. | .. | .. | 4.4540 | "     |
| Lampong       | .. | .. | .. | 3.5410 | "     |
| Penang        | .. | .. | .. | 3.9028 | "     |
| Siam          | .. | .. | .. | 4.2776 | "     |
| Singapore     | .. | .. | .. | 4.5338 | "     |
| Tellicherry   | .. | .. | .. | 4.4421 | "     |
| Trang         | .. | .. | .. | 4.8101 | "     |
| Penang, white | .. | .. | .. | 4.9360 | "     |
| Siam, "       | .. | .. | .. | 5.1441 | "     |
| Singapore "   | .. | .. | .. | 4.6936 | "     |

The pepper of commerce, whole or ground, is therefore a mixture of the different kinds of peppers, and is a condiment which has had a good deal of attention paid it

lately, owing to some successful prosecutions which took place at Liverpool some time ago, when a large quantity of ground pepper was condemned as being adulterated with a material known by the name of *Poiverette*, a hard, tasteless, woody substance, absolutely worthless as a condiment, imported expressly into this country from Italy, for no other purpose than of fraudulently increasing the weight of ground pepper.

It was not, however, wholly owing to the addition of *Poiverette* to pepper that I was induced to undertake the following analysis, although it tended greatly in that direction, but to the great divergency of opinion that seemed to exist amongst various authorities as to the amount of piperine contained in pepper.

The standard works of reference are also at variance with one another, Watts' Dictionary stating that Penang white pepper gave a mean of 5.24 per cent. and Singapore white 9.15 per cent., whilst Singapore black gave a mean of 7.15 per cent.; Sumatra 8.10 per cent. Mr. Heich (ANALYST, vol. xi., p. 188), from 5 to 9 per cent., Mr. Winter Blyth, from 1.8 to 5.5 per cent., Dr. Muter in his "Organic Materia Medica" (third edition), from 2 to 3 per cent., and Ure's Dictionary (sixth edition) a fraction of a grain, and lastly, Dr. Stevenson, in the ANALYST, vol. xii., p. 144, from 6.62 to 7.14 for black pepper, and 6.47 per cent. for white pepper.

Owing, therefore, to such conflicting evidence, with considerable variation in the amount of piperine said to be contained in similar peppers, I determined to investigate the subject myself.

I have done so, and the results obtained in that investigation furnish me with the contents of this paper, and although I have not been able to reduce the limits of variation (but on the other hand to increase them), I have been rewarded by the discovery of the fact that pepper contains a volatile alkaloid, and I have every reason to believe that it is piperidine, from the results I have obtained upon the analysis of its platinum salt:—

|    |    |    |    |       | Found. | Calculated. |
|----|----|----|----|-------|--------|-------------|
| C  | .. | .. | .. | 120.0 | 20.02  | 20.60       |
| H  | .. | .. | .. | 24.0  | 4.32   | 4.15        |
| N  | .. | .. | .. | 28.0  | 5.01   | 4.80        |
| Pt | .. | .. | .. | 197.4 | 33.93  | 33.89       |
| Cl | .. | .. | .. | 213.0 | 36.62  | 36.56       |



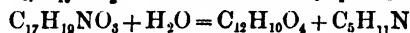
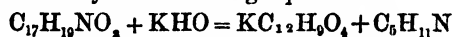
In entering upon this investigation I had in the first place to obtain genuine specimens of pepper, and through the kindness of my friend Mr. Worcester, I obtained from Messrs. Lewis and Peat, well-known brokers in the City, thirteen specimens, and I now take this opportunity of thanking them for their liberality and the trouble they took to obtain them for me.

The samples as received by me were taken from the bulk, that is, dock or cargo samples, and are therefore undoubtedly genuine, and are representative samples of the pepper which is sent to this country, having undergone no particular process of cleaning other than having simply been screened by means of a sieve, containing seven meshes to the inch, before being ground.

Having obtained such magnificent samples, my next consideration was the adoption of a process for the estimation of the piperine, which would give constant and accurate

results, as I had grave doubts as to the accuracy of the alcohol method usually followed, that is, extracting with alcohol and then purifying by potash, and subsequently again crystallising from alcohol.

At this point I therefore directed my attention to the old but well-known fact, that piperine, when treated with caustic potash and alcohol, splits up into piperidine and pipric acid, as represented by the following equation :—



Piperidine, as you are all well aware, is a volatile alkaloid possessing strong alkaline properties (B.P.  $106^\circ \text{C.}$ ), so the idea immediately occurred to me that if the above equation could be made to work in practice so as to yield the theoretical quantity of piperidine, the difficulty would be solved, there being no difficulty experienced in distilling off the piperidine and titrating the distillate with standard acid.

The next thing, therefore, was to prove the above reaction, so having some very fine crystals of piperine in my possession, which I had obtained from Messrs. Macfarlan and Co., of Edinburgh, some years ago, and which I had every reason to believe were pure, but erring on the safe side I re-crystallised them, and subjected various quantities to the action of caustic potash and alcohol.

A series of misfortunes and unsatisfactory results followed, so unsatisfactory that I got quite disheartened, concluded that it was a miserable failure, and allowed the subject to remain at rest for over eighteen months, when fortunately one idle day I again returned to the subject with increased vigour.

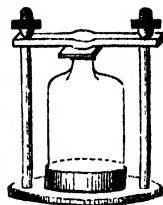
The trouble I had to encounter before was the difficulty of keeping the stoppers of the bottles tight when subjected to heat and pressure, as the digestion was carried on in the water-bath at a temperature of  $100^\circ \text{C.}$

If one was fortunate enough to get them to remain tight under pressure it was 100 to 1 that when allowed to cool, and you attempted to remove the stopper, it would be found hard and fast, no alternative being left but to knock off the neck; otherwise, if it was got out without breaking the bottle, I always found a great loss.

After a dozen bottles had been used up in this manner, not counting the ones that burst, I found that in three instances I had obtained practically theoretical results (which will be seen by referring to the three first estimations in the accompanying table), so encouraged by my results, and at the same time determined to overcome the difficulty, if possible, and make the process a working success, I designed the following little arrangement, with which I have obtained actually theoretical results, which I have tabulated in the diagram before you, the first three estimations, as already stated, having been made in an ordinary stoppered bottle.

| PIPERINE. |         |           |
|-----------|---------|-----------|
| Taken.    | Found.  | Per Cent. |
| ·8400     | ·83075  | 98·89     |
| ·2520     | ·24937  | 98·95     |
| ·5900     | ·58450  | 99·06     |
| ·4320     | ·43170  | 99·93     |
| ·7640     | ·76380  | 99·97     |
| ·5288     | ·52212  | 99·85     |
| ·3530     | ·35197  | 99·70     |
| 1·0108    | 1·01052 | 99·97     |

This instrument, as you will observe, consists merely of an ordinary 4-oz. bottle with its mouth ground flat, and is simply closed by placing a circular piece of sheet india-rubber over it, and then placing it in its holder, putting the clamp in position, and finally making it perfectly tight by screwing down the two screws made for the purpose, put into the water-oven, digested at a temperature of  $100^{\circ}\text{C}$ . for from four to six hours, when the reaction is complete, then removed from the oven and allowed to cool.



When cool it will be found that the bottle has remained perfectly tight, none of the contents having escaped, so all that now remains to be done is to unscrew the clamp, and transfer the contents of digestion bottle to a distilling flask fitted with a condenser, and distil the piperidine and titurate the distillate with standard acid.

Having, therefore, satisfied myself of the accuracy and adaptability of the process, the next thought occurred to me to try the estimation of the piperine contained in the pepper direct, that is, digesting the ground pepper with caustic potash and alcohol for six hours, and then distilling as before.

Ten grms. of ground pepper was carefully transferred to the digestion bottle, 30 c.c. of alcohol added, and then about 3 grms. of caustic potash dissolved in 25 c.c. of water also added, the indiarubber placed in position and the clamp screwed down, and then digested for six hours, allowed to cool, opened at convenience, and contents of the bottle washed into large flask with plenty of water, distillation commenced and carried on until the distillate coming over is neutral, aliquot portions of which are then titrated with  $10 \frac{\text{N}}{\text{H}_2\text{SO}_4}$  using methyl orange as an indicator.

Several experiments were performed in this manner on one sample of pepper, concordant results being obtained in every instance, which established the reliability of the process; consequently all the samples of pepper were treated in this manner, and the results so obtained are tabulated in the table before you.

The piperine estimations having proved successful, I decided to make a complete analysis of the various samples, the results of which I have the pleasure of laying before you this evening.

I will now, therefore, describe in detail the processes employed by me so as to obtain the figures I have placed upon the diagram.

*Moisture.*—The moisture is estimated by the ordinary method of drying a weighed portion of the ground pepper in a platinum capsule at  $100^{\circ}\text{C}$ . in the water-oven until the weight remains constant, and then noting the loss in weight.

*Oil.*—The volatile oil is estimated by distilling 20 grms. of the ground pepper with water in a large flask, shaking the distillate several times with ether, and evaporating the separated ether in a weighed flask at a very low temperature, and finally drying over sulphuric acid.

*Piperidine.*—Twenty grms. of the ground pepper are distilled with water in a similar manner as that for the oil estimation until the distillate is neutral (450 c.c. being about the quantity necessary to distil). An aliquot portion is then titrated with  $10 \frac{\text{N}}{\text{H}_2\text{SO}_4}$  using methyl orange as an indicator. In the piperidine estimation it occurred to me that the process of distilling with water might be done away with, and the pepper

put into a boat and then into a hot-air tube, heated to 230 to 240° F., a constant current of air being aspirated through it all the while, the air ultimately passing through a bulb of standard acid.

Working in this manner, and after an hour's treatment, the acid was washed out of the bulb and its equivalent of soda added, the excess of alkali being titrated back with  $10 \frac{N}{H_2SO_4}$  using methyl orange, as usual, as indicator. The results obtained by working in this manner are interesting on account of only a third of the piperidine being obtained in this way, or rather only a third of that obtained when the pepper is distilled with water.

The following are the results obtained in duplicate when working in the manner just described, using 5 grms. of the pepper:—

| No. Sample | I.    | II.   | III.  | IV.   | V.    | VI.   | VII.  |
|------------|-------|-------|-------|-------|-------|-------|-------|
|            | 0.13  | 0.106 | 0.16  | 0.25  | 0.11  | 0.19  | 0.19  |
|            | 0.13  | 0.105 | 0.12  | 0.25  | 0.10  | 0.20  | 0.17  |
| No. Sample | VIII. | IX.   | X.    | XI.   | XII.  | XIII. | XIV.  |
|            | 0.29  | 0.17  | 0.127 | 0.093 | 0.076 | 0.085 | 0.272 |
|            | 0.25  | 0.17  | 0.127 | 0.093 | 0.076 | 0.085 | 0.271 |

These results tend to suggest that the piperine was to some extent hydrolysed by the action of prolonged boiling with water, but such is not the case for if pure piperine is boiled with water no piperidine is obtained, and it is also disproved by the fact that there is no difficulty in getting the distillate neutral; the amount of piperidine distilled represents a mere fraction of the piperine remaining in the pepper.

I am rather disposed to the theory that there may be a particular ferment contained in the pepper capable of producing the hydrolysis of piperine when boiled with water, or it may be due to the existence of another alkaloid more easily hydrolysed than piperine, anyhow these are the results obtained, and any one is welcome to continue the investigation further if they should feel so disposed

*Ash.*—The dried sample used for the moisture estimation is incinerated at a very low temperature, the most convenient arrangement for this work being a jar-muffle, which is infinitely superior to any kind of burner. The residue obtained is the mineral or inorganic matter, and this in turn is then treated with water and then with dilute acid, so as to obtain the portions soluble and insoluble in those menstrua, the insoluble in acid portion, representing the proportion of sand present, and is of special importance.

*Piperine.*—Ten grms. of ground pepper are digested in a closed bottle similar to that already described, from four to six hours, with 3 grms. of caustic potash dissolved in 25 c.c. of water and 25 c.c. of alcohol. When the digestion is finished, the apparatus is allowed to cool and its contents then carefully washed into a large flask, a few pieces of tobacco-pipe stalks being also put into the flask so as to prevent the violent bumping which would otherwise occur, distillation commenced and continued until the distillate coming over no longer shows signs of alkaline reaction, which is generally the case when about 750 c.c. have passed over. The distillate is then made up to one litre, and titrated as before with  $10 \frac{N}{H_2SO_4}$  using methyl orange as indicator.

*Fibre crude.*—Between 3 to 5 grms. of the ground pepper are placed in a flask and covered with 50 c.c. of dilute sulphuric acid (5 per cent. or 50 grms. of sulphuric acid

per litre), to this 150 c.c. of water are added and the liquid boiled for half an hour, the flask having previously been attached to an upright condenser.

After subsidence, the supernant liquid is run off by means of a syphon into a beaker, and the residue is then twice boiled for half an hour with 200 c.c. of water. After removing as much of the clear liquid as possible, by decantation, the residue, to which is added any sediment that may have become deposited in the beaker containing the acid extract, is next boiled in the same manner with 50 c.c. of dilute caustic potash (50 grms. of KHO in 1,000 c.c.) and 150 c.c. of water for half an hour, and after subsidence the supernant clear liquid is syphoned off into another beaker, and the residue is again extracted by boiling twice with 200 c.c. of water.

The residue obtained after the above process of extraction has been carried out, together with any sediment deposited in the beaker containing the alkaline extract, is now thrown upon a weighed filter and washed well with boiling water, alcohol and ether. The filter and residue are then dried at a temperature of 105 to 110° C. and weighed, and then, in order to ascertain the small proportion of ash which the woody fibre contains, also the accompanying sand, the filter is ignited and the ash found deducted from the previous weight.

This is merely an approximate determination, as the term *crude fibre* designates nothing beyond the fact that it does not consist of pure cellulose, but that a certain amount of ligenous substances are insoluble in acid and alkaline solutions of definite strength, and alcohol and ether, after definite treatment, such as already described, furnishing results which are of some comparative value, but still leaves much to be desired.

*Nitrogen and Albuminoids.*—The nitrogen was determined in the usual manner with soda-lime.

*Alcoholic Extract.*—Two grms. of the ground pepper are extracted for 24 hours with 95 per cent. alcohol.

The pepper under examination is placed in a tube, which in turn is inserted in a Soxhlet's extraction apparatus.

The tubes used for this purpose are ordinary test tubes cut in two, the upper half having a piece of fine linen (previously washed and extracted) tied over the mouth end of the tube, then a wad of extracted cotton-wool of sufficient thickness is placed inside the tube, upon the linen so as to prevent any of the solid particles of the sample finding their way into the receiving flask, and then another wad of cotton-wool is packed on the top of the sample and the whole inserted in the Soxhlet apparatus, and the extraction continued, as already stated, for 24 hours. The alcohol is then distilled off, and the flask dried in the water-oven until weight remains constant.

I must here remark that it is necessary to distil the recovered alcohol with dilute sulphuric acid if it is to be again used for any other purpose, so as to get rid of the piperidine which it now contains.

*Starch.*—Before proceeding to convert the starch into dextrine, the pepper must be carefully extracted with 95 per cent. alcohol, so as to remove substances other than starch which are acted upon by the acid, and also which have the power of reducing Fehling's solution, such as piperine and piperidine, both substances being possessed of the power of reducing Fehling's solution.



The residue contained in the Soxhlet tube is, therefore, readily available for this purpose, having been thoroughly exhausted with alcohol.

Without drying, therefore, it is carefully washed off the cotton-wool into a suitable flask, with about 200 c.c. water and 20 c.c. HCl (sp. gr. 1.121) added, the flask connected with an upright condenser and heated in the water-bath for 3 hours.

After cooling, the liquid is filtered, and the filtrate very carefully neutralised with caustic soda and diluted, so as to measure 500 c.c.; finally titrated with Fehling's solution, and the results calculated to starch or any other desired basis.

A few drops of chloride of zinc may be added, so as to assist clarification of the liquid before filtering.

Extraction with alcohol is indispensable, without which the results are most uncertain and unreliable. Proper and careful extraction with uninterrupted boiling are the two most important conditions to be attended to.

These results, therefore, which I have this evening placed before you, were obtained by the methods I have just described, and although individually I am disappointed with them, I must admit, nevertheless, they are of considerable value, as they are representative analyses of several varieties of pepper, obtained from various quarters of the globe, and as met with in commerce and as shipped to this country.

The moisture and oil determinations are of no practical value, and the same may be said of the piperidine and piperine; the piperidine being in too small quantity to be of any use, the piperine, on the other hand, exhibiting large variations, showing a maximum of 13.03 per cent., with a minimum of 5.21 per cent., and giving a mean of 8.25 per cent.

The albuminoids and matter soluble in alcohol are also of little practical value (except that an excessive amount would reveal the presence of some foreign seed rich in nitrogen), so that we are left with the starch, fibre, and ash as the only data which approaches to anything like reliable, constant, or uniform amount. Fortunately in two of these we have very reliable data, viz., in the ash and fibre. Too great a value, in my opinion, has been placed upon the amount of starch, as will be seen in referring once more to the diagram, a maximum of 42.45 per cent. being obtained, with a minimum of 29.60 per cent., giving a mean of 36.02 per cent. for the black peppers.

It may be of more value in judging white peppers, but as I had only three samples of white, my remarks do not, therefore, apply to white pepper.

An increase of fibre indicates the addition of a more fibrous material than pepper. The fibre will be observed to reach a maximum of 15 per cent., with a minimum of 10 per cent., and a mean of 12 per cent., so that we can easily accept 20 per cent. as a fair basis for calculating the amount of fibrous material.

When we come to the consideration of the ash, however, we have very reliable data, the amount of ash immediately indicating the addition of any material containing a larger proportion of inorganic matter than pepper.

The ash is undoubtedly a most reliable and valuable constituent, and it will be observed that not in a single instance has it reached 5 per cent. If we leave out the Long pepper, we obtain a maximum of 4.65 per cent., with a minimum of 3.51 per cent., and which gives a mean of 3.96 per cent. Anything, therefore, above 5 per cent. must be looked upon with suspicion.

Another valuable indication is the solubility of the ash in water and in hydrochloric acid.

In water we have a maximum solubility of 2.72 per cent., a minimum of 1.41 per cent., with a mean of 1.93; and the insolubility in hydrochloric acid gives a maximum of .62 per cent., with a minimum of 0.06 per cent., and a mean of 0.82 per cent. (Long pepper gives 1.47), so that anything over 1 per cent. of insoluble matter in hydrochloric acid ought to be reported against as containing sand or dirt.

|                | Moisture. | Oil. | $C_9H_{11}N$ | Ash.  | $C_{17}H_{19}NO_3$ | Fibre. | Albumi-<br>noids. | Starch. | Soluble in<br>$C_2H_5O$ . | Undeter-<br>mined. | Total. |      |  | Solubility of Ash in |      |                  |
|----------------|-----------|------|--------------|-------|--------------------|--------|-------------------|---------|---------------------------|--------------------|--------|------|--|----------------------|------|------------------|
|                |           |      |              |       |                    |        |                   |         |                           |                    |        | N.   |  | H <sub>2</sub> O.    | HCL. | SiO <sub>2</sub> |
| Acheen ..      | 15.15     | 1.51 | 0.50         | 3.79  | 12.21              | 10.00  | 2.34              | 42.45   | 0.84                      | 11.21              | 100.   | 1.06 |  | 1.41                 | 1.74 | 0.62             |
| Alleppey ..    | 15.36     | 1.87 | 0.44         | 4.66  | 13.03              | 13.10  | 2.62              | 29.60   | 2.12                      | 17.20              | 100.   | 1.34 |  | 2.72                 | 1.87 | 0.06             |
| Kampoot ..     | 13.82     | 1.63 | 0.55         | 3.51  | 8.13               | 11.65  | 5.37              | 37.50   | 9.57                      | 8.27               | 100.   | 1.42 |  | 1.50                 | 1.70 | 0.31             |
| Lampang ..     | 15.22     | 1.42 | 0.77         | 4.46  | 11.05              | 15.05  | 7.25              | 30.80   | 4.55                      | 9.43               | 100.   | 1.82 |  | 2.15                 | 2.10 | 0.21             |
| Long Pepper .. | 12.26     | 1.56 | 0.34         | 7.57  | 7.15               | 13.75  | 6.93              | 32.10   | 3.50                      | 14.84              | 100.   | 1.51 |  | 2.18                 | 3.92 | 1.47             |
| Penang, W.C... | 15.04     | 0.98 | 0.46         | 4.14  | 6.41               | 11.70  | 8.37              | 41.65   | 5.44                      | 5.81               | 100.   | 1.72 |  | 1.71                 | 1.63 | 0.56             |
| Siam ..        | 14.06     | 1.29 | 0.76         | 3.65  | 6.89               | 12.25  | 6.93              | 40.15   | 6.26                      | 7.76               | 100.   | 1.57 |  | 1.64                 | 1.67 | 0.34             |
| Singapore ..   | 14.72     | 0.99 | 0.72         | 3.64  | 5.72               | 10.75  | 6.31              | 32.18   | 5.55                      | 19.42              | 100.   | 1.40 |  | 2.00                 | 1.48 | 0.16             |
| Tellicherry .. | 14.24     | 1.01 | 0.39         | 3.87  | 8.25               | 12.15  | 5.87              | 33.33   | 2.60                      | 18.29              | 100.   | 1.40 |  | 2.26                 | 1.55 | 0.06             |
| Trang ..       | 14.02     | 1.40 | 0.47         | 3.96  | 5.21               | 10.70  | 6.68              | 37.50   | 4.54                      | 15.52              | 100.   | 1.49 |  | 1.74                 | 1.92 | 0.30             |
| Penang, W. ..  | 14.94     | 0.53 | 0.34         | 2.47  | 8.87               | 4.35   | 2.62              | 51.00   | 0.46                      | 14.42              | 100.   | 0.90 |  | 0.31                 | 1.97 | 0.19             |
| Siam, W. ..    | 13.13     | 1.41 | 0.21         | 2.22  | 7.79               | 4.45   | 6.00              | 53.50   | 0.11                      | 11.18              | 100.   | 1.37 |  | 1.18                 | 0.95 | 0.09             |
| Singapore, W.. | 15.62     | 1.14 | 0.42         | 1.07  | 8.66               | 4.20   | 7.00              | 52.00   | 1.76                      | 8.13               | 100.   | 1.61 |  | 0.30                 | 0.62 | 0.15             |
| Hueks, etc. .. | 12.54     | 1.74 | 0.74         | 16.34 | 6.32               | 22.88  | 6.50              | 11.80   | 4.23                      | 16.91              | 100.   | 1.47 |  | 1.10                 | 6.71 | 8.53             |

## THE WESTPHAL BALANCE.

By W. F. K. Stock, F.C.S., F.I.C.

*(Read at Meeting, January, 1889.)*

IN Mr. A. H. Allen's most valuable and painstaking paper, "On Some Abnormal Samples of Butter" (*ANALYST*, January, 1889), there are some remarks on the Westphal balance which will come as a positive shock to any chemist who may have been too confiding in the performance of an untried instrument.

Mr. Allen did not mention what his balance had cost, but it may safely be said that the cheaper such an instrument is, the more likely will it be to possess defects, for the reason that the actual value of the material used in its construction is as nothing to the labour-cost of its truthful graduation and the accurate adjustment of its weights.

The ease and rapidity with which the densities of liquids can be ascertained at any temperature between 0° and 99·5° C. by the use of the Westphal balance give it a place in the laboratory which nothing else could well supply, and I should very much regret if analysts, and especially the members of this Association, should find it necessary to give the cold shoulder to this handy little machine, for which reason I should like to say a word in its favour. I cannot do this better than by giving my own experience of it. The balance I use was supplied by Oertling, at a cost of three guineas. It has a set of "rider" weights in duplicate. Before taking it into work, I made a rigid inquiry into its performance, thus: The graduations on the beam were measured up by means of a fine springbow divider worked with a screw; the spaces were taken off with a scale of equal parts (by Archbutt) and found to be accurate. The displacement of the plummet in distilled water at 15·5° C. was got on a short-beam balance by Bunge, and the whole of the rider weights were weighed on the same balance, with the beam oscillating, by which means a degree of accuracy beyond the fourth place of decimals was reached.

The following table shows the variations in the riders:—

| Number of Weight. | Weight in Grammes in Air. | Relation to Unity. Plummet displacement = 6·48 grms. |
|-------------------|---------------------------|--|
| 1                 | 6·4806                    | 1·00007  |
| 1a                | 6·4796                    | ·99992   |
| 2                 | ·6482                     | ·10003   |
| 2a                | ·6483                     | ·10004   |
| 3                 | ·0655                     | ·01010   |
| 3a                | ·0655                     | ·01010   |
| 4                 | ·0070                     | ·00108   |
| 4a                | ·0071                     | ·00109   |

|   |    |    |       |
|---|----|----|-------|
| Density of rectified spirit by Westphal | .. | .. | ·8383 |
| " " " Bottle                            | .. | .. | ·8385 |

A glance at the third column of the table will show that the maximum deviation from unity is 1 in the fourth place of decimals, a result which is creditable to the maker, since the balance was supplied in the ordinary way, without any attempt at selection.

The simple law which governs the action of all balances of the Steelyard type tends to aggravate error in direct proportion to the increase of mass in the weight, and the use of rider weights for accurate work on chemical balances lies within very narrow limits, nothing beyond a centigramme being common. In the Westphal balance, however, the whole displacement, which may amount to 10 grms. or more, is called unity, and therefore, unless very palpable imperfections are present, they do not practically vitiate the results; and seeing what can be had at a moderate cost, as in the case of my own purchase, I think there can be no doubt that if another guinea were added to the price, and the extra cost were devoted entirely to the correction of spacing and adjustment of weights, a reliable and trustworthy instrument would be the outcome. The maker could then afford to issue a guarantee with each instrument.

## DISCUSSION.

Mr. ALLEN said the instrument which he had referred to in his paper on "Some Abnormal Samples of Butter" was a Westphal balance, obtained from Messrs. Becker and Co., of Maiden Lane, and, he believed, cost 28s. It was of the ordinary kind sold by that firm. The fault was simply in the inaccurate division of the beam at the eighth point. In other respects it was a perfectly satisfactory instrument, and he had used it for a considerable time with every satisfaction. It must be remembered also that the gravities commencing with the figure 8 were all comparable among themselves, and it was only when it was desired to compare densities obtained by that instrument with those determined by the specific gravity bottle that any discrepancy became important. Still, he had thought it his duty to mention the matter, as he felt that his brother analysts were very probably recording figures in which the same error was involved. He had recently obtained a highly satisfactory Westphal balance from Sartorius, at £2 10s., and also one from Oertling, at £3 3s. Both of these were admirable instruments, and in the case of Oertling's instrument the bearings were of agate, but in both balances the knife edges were of steel. He rather preferred Oertling's balance, as it was intended for use with a 5 c.c. plummet instead of a 10 c.c. plummet, which latter was supplied with the Sartorius instrument.

*(Conclusion of Society's Proceedings.)*

## ABNORMAL BUTTERS FROM IRELAND, DENMARK, AND SWEDEN.

By CHARLES ESTCOURT, F.I.C., F.C.S.

IN April, 1885, a client of mine delivered a sample of Irish butter, duly sealed, and labelled as having been purchased under the Food and Drugs Act.

The Public Analyst for the Borough where the sample was purchased, had condemned it as being a mixture of foreign fat, and my analysis confirmed this result.

## SO-CALLED IRISH BUTTER.

Specific Gravity at 210° F.  
865.1

Insoluble Fatty Acid.  
92.07

The Analyst for the Borough had condemned this upon the result by Reichart. Upon investigating the matter I found that my client had purchased this butter from a very large firm in Ireland, who were, he said above suspicion, one of the firm, indeed, was a member of Parliament.

Certificates for the butter in question had been given by two of the first chemists in Dublin, and it was said even to have passed Somerset House. When the case came before the magistrates however, the Irish firm did not, and my client, acting under my advice would not, ask the magistrates to send the sample to Somerset House.

With the reputation for honesty which all the parties concerned bore, it only needed a possibility of seeing the cows milked, and a supervision of such milking by *inexperienced* persons to prove this "an abnormal sample of butter."

Fortunately, however, under pressure from my client, we obtained the whole secret of the process of manufacture.

Last year's butter was purchased and washed free from all rancidity, churned again with skim milk, oleomargarine, and about 10 per cent. of nut oil, the result being a perfect butter so far as flavour was concerned.

In 1884, two samples of Danish butter were submitted to me for analysis, from one of the boroughs for which I am analyst. I was of opinion that they were adulterated, but before any proceedings were taken, duplicates of the samples were sent to Somerset House, with the result that they pronounced them pure. The following are the analyses :—

|                                | Somerset House. |        | Estcourt. |        |
|--------------------------------|-----------------|--------|-----------|--------|
|                                | No. 1.          | No. 2. | No. 1.    | No. 2. |
| Insoluble Fatty Acid ..        | 89.35           | 88.85  | 89.45     | 88.59  |
| Soluble Fatty Acid ..          | 4.18            | 4.24   | 4.20      | 4.01   |
| Specific Gravity at 210° F. .. | ..              | ..     | 865.70    | 866.0  |

These results would, I am convinced, be now held by all analysts, including Dr. Bell himself, sufficient proof of adulteration. The soluble fatty acids being lower than those even recently obtained by Mr. Allen from his abnormal butters.

It will be remembered that this was before the period when analysts believed that a mixture containing any considerable quantity of butter-fat would pay. It had always been supposed that adding a flavouring of butter-fat to foreign fat was the ordinary method of manufacturing butterine.

In 1885, some clients of mine who are very large purchasers of butter, and have special purchasing agencies in both Denmark and Ireland, and who, I may say, are the largest retailers of butter in Great Britain, brought me a sample of a consignment purchased by their agent in Denmark. The following were the results of the analysis :—

|                                | Dr. Bell. | Mr. Allen. | Estcourt. |
|--------------------------------|-----------|------------|-----------|
| Specific Gravity at 100° F. .. | 908.42    | ..         | ..        |
| Specific Gravity at 210° F. .. | ..        | ..         | 862.50    |
| Insoluble Fatty Acids ..       | 90.08     | ..         | 90.12     |
| Soluble Fatty Acids ..         | 3.48      | ..         | 3.50      |
| Reichart 2½ grammes ..         | ..        | 89         | ..        |

I pronounced this to be a mixture, and both Dr. Bell and Mr. Allen agreed with me.

On reporting the results to my clients, they informed me they had submitted the sample for analysis solely because their buyer had written that "this shipment was poor in quality."

In the face even of these analyses, the producers asserted that the sample was genuine.

In August, 1888, a sample of Swedish butter was received from the butter importer in this country, by the hands of a solicitor at Wigan.

This sample was duly sealed, labelled, and numbered 402 by the Inspector of the Corporation of Wigan.

The analyst for Wigan found that the sample was a mixture, and, on analysis, I agreed with him. When the case came into court, the butter importer asked for the sample to be sent to Somerset House, and this was accordingly done.

On analysis by Dr. Bell and his colleagues, they agreed with us in pronouncing the sample a mixture.

The following are the results of analysis :—

|                             |    | Somerset House. | Estcourt. | Wigan analyst   |
|-----------------------------|----|-----------------|-----------|-----------------|
| Specific gravity at 100° F. | .. | 909.4           | ..        | has been re-    |
| " " 212° F.                 | .. | ..              | 865.5     | quested to give |
| Insoluble fatty acid        | .. | 90.0            | 89.8      | results but has |
| Soluble                     | .. | 3.32            | 3.40      | not done so.    |

Shortly afterwards two more samples, G, N, were delivered to me by the same butter importer, and I found on analysis the following results :—

|                          |    |    | G.    | N.    |
|--------------------------|----|----|-------|-------|
| Specific gravity at 212° | .. | .. | 864.5 | 864.0 |
| Insoluble fatty acid     | .. | .. | 89.7  | 89.0  |
| Soluble                  | .. | .. | 3.53  | 3.57  |

These were reported to be from the same farm as the Wigan 402, and had been analysed by Professor Stein, with the same result as 402.

Later on, the gentleman who represents the Danish agricultural interests in this country, in company with the butter importer, called upon me. I explained to them my view as to the incompleteness of the test of supervision applied at the Swedish farm, whence G and N were taken, and on a suggestion of the agent that it might be essential that I myself should visit the farms, I expressed my willingness to place several days at their disposal.

Having personally supervised the milking of many hundreds of cows of various dairies, I may, without egotism, say that my experience is unique as to the possibilities of fraud or error committed during such operations. Mr. Carter Bell, the analyst for Salford, and two of our Manchester food inspectors, are the only persons having to my knowledge a similar experience.

Shortly after this interview, the gentleman representing the Danish agricultural interests wrote to the Manchester papers explaining how carefully the supervision of the milking had been carried on, from which Professor Stein had obtained his samples G and N.

In reply to this I pointed out that the supervision extended only to the churning of milk, which itself came from no one knew where.

I also stated that no genuine sample of butter from England, Scotland, Wales, and Ireland had yet been analysed giving such abnormal results.

As it seemed incredible that Denmark or Sweden should possess a special breed of cows, or grow naturally special food, in my reply I placed my services for a few days at the disposal of the gentlemen who interviewed me, in hopes that this extraordinary mystery might be unravelled.

From that time until the 3rd of January, 1889, I heard no more of this matter ; then, to my surprise, I saw in the ANALYST the paper on abnormal butters.

From this paper, and the analysis of samples B and O, Danish butter, it appears that we are expected to infer that the samples of Swedish butter, Nos. 402 and G and N, were similar in character to B and O. The analyses negative this assumption at once. While no one would hesitate to pronounce Nos. 402 and G and N adulterated, very few analysts would venture to assert that O and B might not be *abnormal* butters.

The figure for soluble fatty acids is about equal to the lowest figure to be found in Dr. Bell's book, and the specific gravities approach exceedingly near the lowest normal. The visit to Denmark has therefore not materially advanced our knowledge of the butter question. Whatever may be the opinion of analysts with regard to the proof of genuineness of B and O afforded by Mr. Allen's paper, no one can doubt the lack of such proof to clear the Swedish samples from the character of adulterated butters.

And now with regard to the title of Mr. Allen's paper, which appears to me singularly incomplete. If in the syllabus of the meeting of the Public Analysts for December, there had been the slightest indication that the abnormal butter had been Danish or Swedish, I think it probable that very valuable information might have been obtained on this subject, as Dr. Bell, Mr. Betley, of Wigan, and myself, one or all, would in all probability have been present.

And now for the main object of my paper, which is to demonstrate that butter analysis is as reliable as ever, and that so-called abnormal samples of butter have not as yet been proved to be anything more than mixtures.

One cannot help being struck by the phenomenal breed of Danish and Swedish cows, which, according to the information obtained by Mr. Allen, secrete one week perfectly good butter-fat, and without any notice, and without change of conditions, another week produce what an experience of all British butter would lead us to call a mixture.

If this is possible a very serious injustice has been done to the Danish agriculturist by those who are acting in his defence.

The so-called supervision of the milking at these Danish farms was performed by gentlemen whose honour, intelligence, and high ability in the special professions to which they are devoted cannot be questioned. On the ground, however, of their entire lack of experience of the new calling which they have undertaken, I think grave objection might well be taken.

There were five gentlemen to supervise the milking of sixty-five cows at B farm.

Mr. Allen shows exactly the amount of supervision he, with his experience, thought necessary, when he says, the milking, etc., was conducted under the unremitting supervision of the whole party, "*especially of Mr. McGregor and myself.*"

If the party of five could by any possibility have seen sixty-five cows milked *without losing sight of any portion of the milk for an instant* until it was sealed up, then why is it necessary to weaken the effect by singling out as deserving of special remark, "*especially Mr. McGregor and myself*"?

The fact is, I fear, there is not one of these gentlemen who would venture, under cross-examination in a Court of Justice, to declare that *no oily matter could* possibly have been introduced in the milk.

This is especially the case when it is remembered that a very small quantity would if added to the milk make a 20 per cent. adulteration of the butter, indeed one part to 170 parts of milk would suffice. Then, again, the milk should have been creamed at once by the ordinary separator, so that churning could have taken place without leaving the milk all night, which was dangerous, even though it was sealed up. Surely it cannot be alleged that in such well-regulated dairies this apparatus is not known.

From the foregoing remarks it will be evident that fraud might have been committed. I do not assert it was so committed. I do say, however, that the agent of the Danish Agriculturists in England has done the farmer a serious injustice in not completely proving the impossibility of fraud. This is, indeed, very necessary when it is remembered that nearly all the mixtures which have been condemned in this country have been alleged to be Danish or Swedish, and I trust the Local Government Board or the Board of Trade will cause a complete investigation of the whole question to be made at an early date, so that analysts may reach finality in their inferences from butter analysis.

I have only one word more to add, it is in connection with Mr. Allen's apparent wish to show that the specific gravity of B and O are normal.

This is effected by finding fault with our old friend Westphal, which instrument, since I first introduced it for ascertaining the specific gravity of liquids at high temperatures, has been of great value to the analyst.

Mr. Allen should have given figures for, say, beef-fat taken under the same condition as butters B and O, using the faulty division eight, of the Westphal. I give them below, so that it may be seen that there is a good margin by the gravity process between butter-fat and ordinary fat, viz.—

|                                    |    |    |       |
|------------------------------------|----|----|-------|
| Butter O, specific gravity at 212° | .. | .. | 866.3 |
| Beef-fat, specific gravity at 212° | .. | .. | 859.6 |

It would also have been most valuable information if Mr. Allen could have given the gravities of beef-fat and butter-fat by the specific gravity bottle used by Professor Stein.

One word more regarding the Reichart method, which has always met with such favour at the hands of Mr. Allen, and which I am informed is the one almost, if not exclusively, relied upon by Professor Stein for his daily examination of butter. I desire to call attention to the paper by Dr. Wollny in the January and February numbers of the ANALYST for 1888. In page nine, experiment 135, Dr. Wollny gets 20.45 c.c., as the Reichart of a genuine butter. On page ten, the explanation of this extraordinary result is given, and this explanation together with the possible sources of error (one possible error is, we may get minus 30 per cent. from cohesion of fatty acids) which Dr. Wollny points out upon page forty, would be sufficient to cause us even now considerable doubt as to the reliability of the process.

In conclusion, the inference, I think, which may fairly be drawn from the foregoing remarks is that the specific gravity method either of Dr. Bell or myself, and the Angell-Hehner insoluble and soluble fatty acid determination, as modified by Dr. Muter and others, are still the most reliable methods for determining the genuineness of butter.



# COLLECTED DETAILS OF SO-CALLED ABNORMAL BUTTERS.

|  | SOMERSET HOUSE.   |                     |                   |                           | ESTCOURT.            |                     |                   |           | ALLEY.            |                     |                   |                   |
|--|-------------------|---------------------|-------------------|---------------------------|----------------------|---------------------|-------------------|-----------|-------------------|---------------------|-------------------|-------------------|
|  | Specific Gravity. | Insol. Fatty Acids. | Sol. Fatty Acids. | Reichert.                 | Specific Gravity.    | Insol. Fatty Acids. | Sol. Fatty Acids. | Reichert. | Specific Gravity. | Insol. Fatty Acids. | Sol. Fatty Acids. | Reichert.         |
| Danish Butter, 1884. 1. ...                      | Not given.        | 89.35               | 4.18              |                           | At 210° F.<br>865.70 | 89.45               | 4.20              |           |                   |                     |                   | 2.5 grms. Butter. |
| " " 2. ...                                       |                   | 88.85               | 4.24              |                           | 866.00               | 88.59               | 4.31              |           |                   |                     |                   |                   |
| Irish Butter, 1885. ...                          | ..                | ..                  | ..                | ..                        | 865.10               | 92.07               | ..                | ..        | ..                | ..                  | ..                | 7.60              |
| Danish Butter, 1885. ..                          | 908.42 at 100° F. | 90.08               | 3.48              |                           | 862.50               | 90.12               | 3.50              |           | ..                | ..                  | ..                | 8.9               |
| Swedish Butter, 1888. }<br>Wigan, No. 402. ... } | 909.4             | 90.00               | 3.32              |                           | At 212°.<br>865.5    | 89.80               | 3.40              |           | PROF. STEIN.      |                     |                   |                   |
| Swedish Butter, G, 1888. ...                     | ..                | ..                  | ..                | ..                        | 864.5                | 89.7                | 3.53              | 23.60     | ..                | ..                  | ..                | 24.2*             |
| " " N, 1888. ...                                 | ..                | ..                  | ..                | ..                        | 864.0                | 89.0                | 3.57              | 22.55     | 866.0             | ..                  | ..                | 23.9*             |
| Danish Butter, B, 1888. }                        | 909.9             | 90.00               | 4.50              | Not enough of the sample. | ALLEN.               |                     |                   |           | 864.0             | 90.43               | 4.44              | 5 grms. 22.39     |
|  |                   |                     |                   |                           | 866.30               | 89.8                | 4.70              | 24.64     |                   |                     |                   |                   |
| " " O, 1888. }                                   |                   |                     |                   |                           |                      |                     |                   |           | 864.10            | 90.10               | 4.67              | 24.70             |

NOTE.—At my request, made on reading the paper upon "Abnormal Butters," Mr. Allen promised to let me have samples of B and O, if any portion was still left. Accordingly, I received an original sealed sample of O, and a small quantity of the rendered fat of B.

\* The specific gravities of Prof. Stein are abnormally high, compared with Reichert, of the samples G and N and B and O.

## ON SOURCES OF ERROR IN DETERMINATION OF NITROGEN BY SODA-LIME, AND MEANS FOR AVOIDING THEM.

By W. O. ATWATER.

*(Continued from page 18.)*

Five series of trials were made. Previous experience had persuaded us that when (1) the tubes are of moderate length and compactly filled with soda-lime, (2) only a moderately high heat is used, (3) the combustion does not proceed too slowly, and (4) the flames are turned off and the tube allowed to cool slightly before aspirating with air, there is no considerable loss of nitrogen by either dissociation or oxidation. In the first series, in which the operation was conducted in the usual way, a confirmation of this impression was sought. In the second series the effect of increasing the length of the tube and with it the time of sojourn of the ammonia gas in the tubes, without increasing the heat, was observed. In the third series the effect of high heat was tested by using long tubes as in the second series, and making the heat much greater. In the fourth series it was sought to learn whether the loss of nitrogen observed in the third series was due to dissociation or oxidation or to both. The trials of the fifth series had a similar object. The results are given in detail in Table II., which includes all the determinations made, and are recapitulated in Table III.

The figures of the first series indicate that with tubes of our ordinary length, 40 cm. or a little less, compactly filled (about 16 cm. with mixture of fine soda-lime and substance, 4 cm. with "rinsings" of fine soda-lime, and 12 cm. with an anterior layer of coarse soda-lime), at a heat sufficient to make the tube dull red, designated here as "medium," and with aspiration by air after the tubes had begun to cool, there was no loss of nitrogen.

In the second series the tubes were long enough to make the anterior layer of coarse soda-lime about 35-40 cm.; the charging otherwise was the same as in the first series. The percentage of nitrogen obtained was the same. Lengthening the tube had no effect upon the result. At moderate heat there was no loss by dissociation with closely-

TABLE III.

*Recapitulation of Determinations of Nitrogen in Ammonium Sulphate under Different Conditions.*

| Series. | Length of Tube and Anterior Layer of Soda-lime. | Heat of Combustion. | Aspirated with. | Nitrogen found. |                     | Loss of Nitrogen in per cent. of total Nitrogen. |              |
|---------|---|---------------------|-----------------|-----------------|---------------------|--|--------------|
|         |   |                     |                 | Average.        | Range of Variation. | Maxim'm.   | Average.     |
| 1st     | Usual.*   | Medium.             | Air.            | Per cent. 21.12 | Per cent. 0.03      | Per cent. ..                                     | Per cent. .. |
| 2nd     | Very long.†                                     | Medium.             | Air.            | 21.12           | 0.01                | ..   | ..           |
| 3rd     | Very long.†                                     | High.               | Air.‡           | 20.83           | 0.06                | 1.5  | 1.4          |
| 4th     | Very long.†                                     | High.               | Hydrogen.       | 20.83           | 0.21                | 2.0  | 1.4          |
| 5th     | Very long.†                                     | Medium.             | Hydrogen.       | 21.11           | 0.03                | ..   | ..           |

packed tubes, even when the latter were very long and the exposure of the ammonia to the heat was increased.

\* Tube about 40 c.m., anterior layer of soda-lime about 12 c.m.

† Tube 75 c.m., anterior layer about 35-40 c.m.

‡ In one case with carbonic acid.

In the third series the conditions were the same as in the second, except that the temperature was made as high as the tubes of the most difficultly fusible Bohemian glass we could obtain would endure without bursting. The standard acid employed was rather concentrated, so that but a small quantity was needed in the nitrogen bulb, and the internal pressure was thus reduced to a minimum. It was thus possible to heat the tubes to bright redness without their bulging. Instead of 21.12, only 20.83 per cent. of nitrogen was obtained. This falls short of the actual amount by 0.29 per cent. of the weight of the sulphate of ammonia, or 1.4 per cent. of the total nitrogen. The indication of loss by either decomposition or oxidation of ammonia was very apparent.

In the fourth series the conditions were the same as in the third, except that air was excluded, the object being to find, if practicable, how much of the loss in the previous series was due to the burning of ammonia by the oxygen of the air, and how much to dissociation. In No. 10, the length of the tube was actually 80 cm. instead of 75 cm. as in the other cases. The extra 5 cm. of the posterior end were filled with bicarbonate of soda, which was heated at the beginning of the experiment to expel the air present in the tube, and again at the end to drive out the residual ammonia. In Nos. 11 to 14, as in all of the next series, in which hydrogen was used for the same purpose, the tubes were about 80 cm. long or a little longer, the extra 5 cm. at the posterior end being filled with asbestos. The hydrogen, which had been dried by sulphuric acid, was passed through the combustion tube for three quarters of an hour, and the tube was then exhausted by a mercury pump, after which hydrogen was again passed through for half an hour. Assuming that the air had thus been very nearly all removed, the combustion was conducted at the very high heat, as in the third series. When it was done, hydrogen was again passed through to wash out the residual gases, precautions being taken to admit no air. The amount of nitrogen obtained averaged the same as in the third series, 20.83 per cent. The exclusion of air made then no difference in the result. This indicated that the loss was due not to oxidation, but to dissociation of ammonia.

It is observable, furthermore, that the individual results in the third and fourth series vary considerably, the range in the fourth series being .21, while in the first and second series it was only .03 per cent. While the agreement of duplicates is a very uncertain evidence of the correctness of an analysis, a wide disagreement may be regarded as a tolerably sure indication of error.

In the fifth series the conditions were the same as in the fourth, except that the combustion was made at "medium" heat. The results, which average 21.11 per cent., are practically identical with each other and with those of the first and second series. The difference in condition between this and the fourth series, like that between the second and third, is simply one of heat, and that difference in each case evidently makes the whole of the difference in result.

To resume:—In every case in which the medium heat was employed, whether with long or with short tubes, whether with or without air, the full amount of nitrogen was obtained. In every case with the high heat there was a loss from 1 to 2 per cent. of the total nitrogen in the substance. Neither the length of the tubes nor the presence or absence of air made any difference in either the amount of nitrogen obtained or the uniformity of the results, but the high heat materially reduced the amount of nitrogen and made wide variations in results of duplicate determinations.

That more definite statements as to temperature at which the dissociation takes place are to be desired, goes without saying. Ramsay and Young,\* in a series of very interesting experiments on the temperature of dissociation of ammonia, find that the point at which it commences varies greatly with the nature of the surrounding medium.

\* *Jour. Chem. Soc.*, 1884, Proc. p. 88.

In a porcelain tube filled with broken pieces of porcelain, in an iron tube filled with porcelain, and in a glass tube filled with ignited "porous" asbestos cardboard, to expose the gas to a large surface, the decomposition commenced at about 500° or below. At 500°-520°, however, it was very small, but increased gradually at higher temperatures. In contact with a glass surface the temperature at which decomposition begins was much higher. The nature of the surface heated has a very great influence on the amount of ammonia decomposed. In a plain dry iron tube the decomposition was apparently complete at 780°, but if water was present only 95 per cent. was decomposed. At 760°, in a glass tube containing iron wire, 64.3-76 per cent. of the ammonia was decomposed; but when copper was substituted (the other conditions remaining essentially unaltered) only 2.0 per cent. was decomposed. The authors find that "the amount of decomposition depends partly upon the rate of passage of the gas, or, in other words, on the time of exposure to heat," and that "the extent of surface also influences the amount of decomposition."

(To be continued.)

#### LAW NOTES.

**HEAVY PENALTY FOR ADULTERATED MILK.**—At Wolverhampton Police Court on January 30th, before Mr. Neville (stipendiary)—F. W. Vickers, Tissington, Ashbourne, Derbyshire, was charged with selling adulterated milk.—Mr. Brevitt (town clerk) prosecuted, and said that the difficulty the prosecution had had in this case was to secure the person who, under the Act, was really liable for the alleged adulteration, and, if the defendant were convicted, he must ask for a substantial penalty.—Inspector Blanton deposed that on January 2nd, from information received, he went to the London and North-Western Railway station at Wolverhampton, and saw a churn of milk containing twelve gallons. It bore a warranty label, and was consigned from Ashbourne to the Midland Dairy Company, Horseley Fields. Witness took a sample from the churn, and had it analysed by Mr. E. W. T. Jones, the borough analyst, who certified that it contained 19 per cent. of water.—Mr. Paine, for the defence, urged that the defendant had received no notice from the prosecution of their intention to test the milk, nor had he received a sample from them.—The Stipendiary said he thought it would be fairer to the defendant in future if a sample were supplied to him after it had been taken by the prosecution, although *there was no legal obligation upon them to do so*. It was satisfactory that the original vendor of the milk had been found and proceeded against. In justice to the milk-sellers in the town, he must impose the full penalty under the Act—namely, £20, and costs.

**ADULTERATED PEPPER.**—At Glasgow Sheriff Court on the 14th ult. Matthew Kerr, grocer and provision merchant, 61A, King Street, Calton, was charged before Sheriff Balfour, at the instance of Mr. Peter Fyfe, sanitary inspector, with having, on 19th December, sold to Mr. Robert Inglis, assistant sanitary inspector, a quarter pound of black pepper, which on analysis was found to contain 3 per cent. of sand, 4 per cent. of mineral matter, and 7 per cent. of pepper husk, all of which are extraneous to whole pepper. The respondent pleaded guilty. His agent, Mr. Wm. Shaw, writer, stated that Mr. Kerr bought the pepper from a house in Glasgow which held a guarantee from a Liverpool house that the pepper was pure. It was what was known as Penang pepper, which had naturally a large amount of impurity in it. After hearing a further statement from Mr. Shaw, Mr. R. G. Ross, writer, who prosecuted, and Dr. Tatlock, the analyst, his Lordship gave judgment. The Sheriff said that he thought Mr. Kerr had been well advised in tendering a plea of guilty. It appeared that black pepper had got a core and an outside husk, and in preparing it for the market there must be to a greater or a lesser extent a certain quantity of sand and mineral matter adhering to the pepper. Dr. Tatlock had taken the Somerset House standard, which allowed a percentage of 3½ of sand, and in regard to mineral matter he had been guided by public analysts and writers of authority, who allowed 7 per cent. for mineral matters, and as long as the percentage of sand and mineral matter only came to 3½ and 7, no prosecution would be directed against any party who sold black pepper. But the line must be drawn somewhere. From the manner in which this black pepper was prepared, it was perfectly clear that the pepper berries, after being dried, must have particles of earthy matter adhering to the husks, and if black pepper were sent over to this country with an immense proportion of earthy matter adhering to the husks, with the intention of being sold in that way, it would not do to allow such a sale to take place, because the earthy matter might get in, not by fair, but by foul means. To prevent that the Somerset House and those public analysts and writers of authority had fixed what he presumed were reasonable and fair standards. Dr. Tatlock had acted most liberally in stating the adulteration, because, in point of fact, the mineral matter really amounted to about 16 per cent., and the sand to about 6 per cent. It was not to be supposed that in inflicting a light penalty, as he was going to do, he by any means countenanced black pepper being sold in the state in which Mr. Kerr had sold it. But he had no reason to doubt Mr. Kerr's *bona fides* in the matter. He apparently bought from a wholesale house, who, on their part, held a written guarantee from the foreign sellers. Mr. Kerr, unfortunately, had not been armed with such a written guarantee, and he was therefore liable to the authorities for selling the adulterated article. As it was the first case of the kind that had been brought before him, the Sheriff, in the circumstances, inflicted a penalty of 15s. The fine was paid.

## CORRESPONDENCE.

[The Editor is not in any way responsible for opinions expressed by his correspondents.]

To the Editor of the ANALYST.

SIR,—As few penalties for adulteration are inflicted, the enclosed report\* may interest your readers, especially as the case comes under the special provision of the Act for procuring milk for analysis at the railway station, or in course of delivery. The following are the analytical results of this sample of milk:—

|   |     |     |     |     |        |           |
|---|-----|-----|-----|-----|--------|-----------|
| Specific Gravity at 60° F.  | ... | ... | ... | ... | 1025.7 |           |
| Total Solids  | ... | ... | ... | ... | 9.93   | per cent. |
| Fat (by Adams' Coil method)   | ..  | ... | ... | ... | 3.03   | "         |
| Solids not Fat (by difference)  | ... | ... | ... | ... | 6.90   | "         |
| " " (by Bell's method)  | ... | ... | ... | ... | 7.29   | "         |
| Ash   | ... | ... | ... | ... | 0.63   | "         |
| Lactose (C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ) by Polariscope | ... | ... | ... | ... | 3.60   | "         |
| " " by Fehling  | ... | ... | ... | ... | 3.54   | "         |

Yours truly,

E. W. T. JONES,

Public Analyst for Staffordshire, etc.

## A MARE'S NEST.

SIR,—Now that the Society of Public Analysts have appointed a *Select Committee* (which for brevity's sake we shall term the A B C of the Society) to investigate the subject of Butter Analysis owing to the supposed alarming state of matters brought about by Mr. Allen's late paper, entitled "Abnormal Samples of Butter," it may be of interest to the members of the A B C to know that as far back as the year 1884, Professor Wiley of Washington, in analysing nine samples of genuine butter found as a minimum for insoluble fatty acids 88.50, and a maximum of 89.89 per cent., the first figure being Angell and Hehner's highest figure.

In the year 1886, Professor E. Waller, of New York, found 90.26 per cent. as a maximum, and 86.40 as a minimum for twenty-six genuine butters examined by him; and in the same year Professor C. B. Cochran found 87.7 per cent. as his highest figure, and 86.7 as his lowest figure in twenty-five genuine Pennsylvania butters, figures which prove conclusively that it is not only in Danish Butters that high percentages of insoluble fatty acids are to be found. The figure 89.89 is as near as a touch to 90 per cent. (and we all know what as near as a touch means), a figure obtained in the year 1884, the difference between 89.89 and 90 being less than the difference between the figures obtained by Mr. Allen in his two analyses which were performed in duplicate, and by a strange coincidence Professor Waller's highest figure 90.24 obtained in 1886 coincides with one of Mr. Allen's estimations.

Is it possible that the A B C are ignorant of these facts!—Yours, etc.,

THE GREAT I AM.

## TO CORRESPONDENTS.

F. A. B.—Had you applied some years ago you might possibly have gained admittance without examination, but, so far as we know, such days are now over. We are not aware that there is any relaxation of the rule as to the fixed course of study, and, moreover, we fear that, even if there were, the examination itself would present an insuperable barrier to a man in business who had not time to go through a special course. That this should be so is only just, because it is intended to exclude all but those who really make an actual profession of chemistry as distinct from pharmacy. Undoubtedly some pharmacists have managed to get in at present, but, as they die off, their places are not likely to be filled up by others of the same *status*, because a man who became a practising consulting chemist would naturally drop the shop altogether, it being impossible to combine the two businesses, which are totally distinct in every respect.

PROF. KINNICUTT.—Letter to hand but no paper arrived yet (February 25th). When it comes will make use of it as soon as possible.

Communications on Literary or Exchange Matters to be sent to 325, Kennington Road, London, S.E.

\* See Law Notes.

# THE ANALYST.

APRIL, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

AN ordinary meeting of the Society was held at Burlington House on Wednesday, 13th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

On the ballot paper being examined, it was announced that the following were duly elected :—As member, E. W. Voelcker, F.I.C., F.C.S., Analytical Chemist, London. As associate, J. S. Ford, Assistant to Professor Crum-Brown, Edinburgh.

Mr. W. Dibdin, Chemist to the Metropolitan Board of Works, was proposed as a member.

The following papers were read and discussed :—

“Notes on Lactose,” by E. W. T. Jones.

“Colouring Matter (Arsenical) Used for Colouring Candles,” by W. F. Lowe.

“Methods of Fat Extraction in Milk Analysis,” by Dr. Vieth.

A new apparatus for use in Butter Analysis was exhibited and explained by Mr. H. Droop Richmond, and Dr. Vieth also explained the apparatus he uses for the same purpose.

The next meeting of the Society will be held at Burlington House on Wednesday, the 10th inst.

## AN IMPROVED METHOD FOR THE ANALYSIS OF FATS AND OILS.

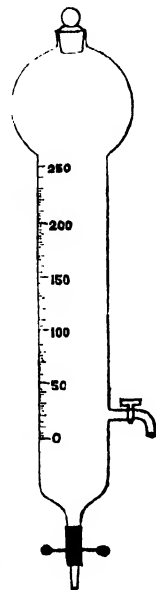
BY JOHN MUTER, PH.D., F.R.S.E., F.I.C., & L. DE KONINGH, F.I.C.

(Read at the Meeting, February, 1889.)

### INTRODUCTORY.

IN the year 1878 the senior author of this paper contributed to the Society of Public Analysts a method for the estimation of oleic acid in fats and oils. This process was based upon the formation of an absolutely neutral oleate of lead, solution of the salt in ether, and decomposition of the same in a special apparatus by means of hydrochloric

acid. The apparatus then described has since been rather extensively used, and is figured in the various price lists as "Muter's Olein Tube." It has since undergone considerable alterations, and, as it plays a prominent part in the method now about to be described, we give, to commence with, a fresh description of the tube as now employed. From the illustration in the margin (which is not to scale, and is too wide in proportion to the length) it will be seen that it is essentially a burette with a bulb at the top, and provided with a well-ground stopper. The graduated part is of such a width as to distinctly show 1 c.c. in the graduations, and it has a stop cock at a height of 50 c.c. from the bottom. The graduations commence at 40 c.c. from the lower end, and continue up to 250 c.c., ending just below the bulb. In winter the tube can be used in a clamp attached to an ordinary retort stand, but when the temperature of the laboratory exceeds 60 F., it may be arranged in an outer jacket, which can be kept filled by running water, or some other means may be taken for keeping the temperature low and fairly equal during the whole progress of an operation. This jacket is not shown in the drawing, but any chemist will easily see how it should be fitted. We are not aware that the improved tube can be got anywhere but from Cetti's, of Brooke St., Holborn (who make them for us); but no doubt they will shortly become as general in the price-lists as the former pattern. In the remarks that follow, this apparatus will be henceforth referred to as the "olein tube," and having thus got quit of any further necessity for referring to it in detail, we proceed to our main subject.



The remarkable advance rendered possible in fat analysis by Hübl's discovery of the iodine absorption method has opened up a large field of research, which is now being actively worked by many experimenters. It will be readily admitted by all analysts that in dealing with the power of fats to absorb iodine, three factors come into play, viz. —

- (1) The difference in the iodine absorbing power of oleic and linoleic acids.
- (2) The joint amount of these acids actually present in the fat.
- (3) The ability to *always* perform the process in the presence of an *excess* of iodine that shall be as nearly constant as possible.

If, therefore, we can first isolate the fluid acids of any fat, and having found the actual amount of such acids present in the sample, submit them to the action of the iodine under fixed conditions and, *without having risked any chance of an alteration in their nature during the process of isolation*, it is evident that we have attained a distinct step in advance of our present methods. Up till now we have been unable to find any published process for the estimation of the fluid acids of a fat without their having been exposed to the air, dried by heat, or a change in their nature otherwise rendered possible by the method of isolation employed. Before such a process could be devised, it was necessary to prove two points. (1) Can the amount of the acids be found directly from their ethereal solution with fair accuracy? (2) Can the iodine be applied to the acids without any previous exposure to the air, and consequently to oxygen? Experiments have proved that both these points are quite attainable. It is

not our purpose to overload our paper with a tedious account of such experiments, because it is a matter that any analyst can easily verify for himself. We will therefore content ourselves by saying that a comparison of the results of our process, with those obtained by the gravimetric method in the case of fats so widely different in their nature as tallow and linseed oil, has proved the sufficient accuracy of the volumetric process hereafter detailed, for the purpose for which it is intended. There is little doubt but that the prolonged use of the process, side by side with gravimetric methods, will ultimately throw light on the respective combining weights of oleic and linoleic acids, when we venture to think that it will be found that there is not so great a difference as is at present supposed to exist by many authorities. All such speculations are, however, foreign to the purpose of our present preliminary paper, and must be reserved for a future occasion. At the moment, our intention is simply to give our method of working, and to leave the consideration of its various possible applications to future papers. The subject of the analysis of lard and butter being very pressing matters at present for public analysts, we are dealing with them first, and will give the results of such investigation after describing the details of the main process.

#### THE PROCESS.

A flask of suitable capacity is counterbalanced, and about 3 grms. of the oil or fat having been introduced, the weight is ascertained. To this are added 50 c.c. of alcohol and a fragment of solid potassium hydroxide sufficiently large to saponify the fat. The mouth of the flask having been closed by a cork, through which passes a long tube drawn out to a fine point, the whole is heated on the water bath until the fat is thoroughly saponified. A drop of alcoholic solution of phenol-phthalein having been added, acetic acid is dropped in until the solution becomes faintly acid, and then alcoholic potash is carefully stirred in until the *very faintest* pink tinge is restored. With certain oils the solution will be too dark for the use of the indicator in this manner, and in such cases it must be applied in the form of phenol-phthalein paper. 200 c.c. of boiling distilled water are then placed in a 500 c.c. basin, 30 c.c. of a 10 per cent. solution of plumbic acetate are added, and the whole brought to the boil. Into this the soap solution from the flask is slowly poured, with constant stirring, and the whole is allowed to cool slowly, stirring well so as to cause the precipitate to agglomerate; and the clear liquor is poured off. Boiling water is immediately poured on, and the precipitate is rapidly washed by decantation. When the washing is complete, the precipitate is scraped from the basin into a stoppered bottle, and 80 c.c. of *redistilled* ether having been poured upon it, the remaining particles of the precipitate are washed from the basin into the bottle with ether, and the bulk of ether in the bottle is finally made up to 120 c.c. The bottle is securely closed and allowed to stand for twelve hours (with occasional shaking), during which time the plumbic oleate will entirely dissolve. A funnel with a ground edge is then arranged over the "olein tube," a filter is placed therein and the contents of the bottle having been filtered into the tube, the insoluble plumbic stearate, etc., remaining on the filter, is washed with ether until the washings pass free from lead. This will usually be attained by the use of 100 c.c. of ether, and during the filtration and washing the funnel must be kept covered by a ground glass plate. The funnel having been removed, dilute hydrochloric acid is poured into the tube up to the first mark (thus using



about 40 c.c. of acid, 1 in 4), and the tube having been closed by the stopper and taken from the clamp, is thoroughly shaken until the decomposition is complete, which is indicated by the ethereal solution clearing up. The tube having been put back in its support, the liquids are allowed to separate and the aqueous layer is run off by the bottom pinch cock. Water is then poured in up to the same mark, the whole is again shaken and separated as before, and this is repeated until the washings are drawn off free from acidity. Water is then once more run in until the ether is forced up to the zero mark, and ether is added (if necessary) so as to bring its upper layer to a definite point (say 200 c.c.), and the total volume is read off and noted. 50 c.c. of the ethereal solution of the fluid acids are run into an Erlenmeyer's flask, and the flask having been attached to a condenser, the ether is distilled off by a bath of warm water until only a little remains. It is important that the whole of the ether should not be distilled off, so as to avoid contact of the acids with the air. 50 c.c. of pure alcohol (or methylated spirit that has been rectified over potassium hydroxide) are added to this residue, and the solution is titrated with deci-normal soda, using phenol-phthalein as indicator. Each c.c. of soda used represents .0282 of oleic acid, and the amount found is calculated up to the total bulk of the ethereal solution, so as to obtain the total fluid acids in the weight of fat started with.

Having thus ascertained the total acids, and also the strength of the remaining ethereal solution of the same in the "olein tube," the next step is to run off as many c.c. of that liquid as will contain .5 gram. of oleic acid (or as nearly that quantity as can be conveniently measured by means of the instrument, of course carefully noting the amount taken) into a stoppered bottle of at least 350 c.c. capacity, and to immediately close the mouth of the same by a cork through which passes two tubes, the one going down nearly to the surface of the liquid, while the other just passes through the cork. The long tube is then connected with a gas apparatus, in which carbonic anhydride\* is being generated from marble and hydrochloric acid, and the gas washed by passing it through a solution of sodium bicarbonate, and then dried by passing it over fused calcium chloride. The bottle is placed in water at about 120° F., and a rapid stream of gas is passed through until *every trace* of the ether has evaporated. To the residue 50 c.c. of *Hübl's reagent* is instantly added, and the stopper having been at once inserted, the bottle is put aside in an absolutely dark cupboard for twelve hours. A blank experiment is, as usual, started in another similar bottle with the same amount of Hübl's reagent, and set to stand side by side with the other bottle. At the expiration of the proper time, 35 c.c. of 10 per cent. solution of potassium iodine are added to each of the bottles, and the contents having been made up to 250 c.c. with water, 15 c.c. of chloroform added, and the whole shaken, both are titrated in the usual manner with a deci-normal solution of sodium thiosulphate (hypo) that has been just previously standardised with an accurate deci-normal iodine solution. The difference between the amount of "hypo" consumed by the check and the experiment respectively, gives the amount of iodine

\* NOTE.—When the paper was read it was stated that ordinary gas had been successfully employed, but since that we have preferred the arrangement now detailed. It is very important that the volume of the ether should not alter between the running off of the first 50 c.c., and the taking of the amount representing the .5 gram. of acid. If it cannot be maintained by regulating the temperature, the volume remaining after taking the 50 c.c. must be noted, and then again renoted before taking off the second quantity, and corrected by calculation.

absorbed by the weight of oleic acid taken, which is then calculated to the amount required by 100 grms. and put down as the "iodine absorbing power" of the fluid acids of the fat under examination.

Such therefore is the process, and by it we not only obtain the amount of fluid acids present in the fat with a fair amount of accuracy, but we also believe that a reasonably constant iodine number for the acids from each fat can be determined when in a reasonably fresh condition, thus enabling us to calculate the amount of any admixture with a very much more tolerable amount of certainty than has hitherto been attainable. We invite our colleagues to try the method, and to assist us in establishing reliable iodine numbers for the acids from every oil and fat. Meantime we are going on with such an investigation, and will continue to submit the results, as rapidly as possible, in the pages of the ANALYST. As being at the moment the most interesting to public analysts, we have commenced with some solid fats used for food.

*(To be continued.)*

## DENSITY.

BY H. DROOP RICHMOND.

*(Read at Meeting, February, 1889.)*

WHEN we talk of the density of a body we mean the mass of a unit of volume of that body, or, as the unit of mass has been fixed at 1 grm., and the unit of volume at 1 cubic centimetre, the number of grms. in 1 cubic centimetre; thence it follows that density is not a relative, but an absolute property. Notwithstanding that the cubic centimetre has been fixed as the volume of 1 grm. of water at 4° C. (the point of maximum density), a custom has sprung up of assuming that an instrument for taking density graduated to hold  $x$  grm. of water at 15°, 15.5°, or 16° C. (as the case may be) holds  $x$  cubic centimetres; this arbitrary creation of units of volume, besides being clearly wrong, is liable to create confusion, and renders the expression of results uncertain, which uncertainty is not removed entirely by the use of such an illogical expression as "the density at 15° compared with water at the same temperature." To compare an absolute quantity is absurd; this uncertainty is much less, however, than that caused by errors of observation, many of which are not even noticed, much less corrected.

I do not propose to discuss either the taking of densities of either gases or solids, on account of the special methods and precautions against errors, which are so well known in the case of gases, and of the comparative unimportance attaching to the determination of the densities of solids; my remarks must therefore be taken as applying to liquids only.

We use practically three methods for determining the densities of liquid:—1. By hydrometers. 2. By the measurement of the loss of weight of a solid in a liquid, *e.g.*, the Westphal balance and the torsion balance. 3. By the determination of the mass of known volume, *e.g.*, the pycnometer.

1. Hydrometers.—The faults of these instruments consist in errors introduced by the cohesion of the liquid to the material of which the instrument is made, which render it difficult to read off the exact point which is at the level of the surface of the liquid; as also the volume of the portion immersed is determined in part by the cohesion, it follows that hydrometers do not give the same reading in different liquids, whose density may be the same, if the viscosity is different. Another error is caused by expansion by heat if the hydrometer is used at a different temperature than that for which it was graduated. Their merits consists in speed, and if they are graduated for

use in one particular liquid, and at a pretty constant temperature, fairly exact results are obtainable (within '0005).

2. Instruments which measure loss of weight in a liquid.—Of these the Westphal balance is the most important and widely used, and is extremely quick and convenient, where great accuracy is not required, though open to grave errors. Its faults are the errors due to cohesion (very slight); to the difference between true weight and apparent weight in air; to the condensed film of air on the plummet, which is, however, removed on immersion in most liquids; to the unequal expansion of plummet and liquid of which the density is to be taken at any other temperature than that for which the instrument is set, and of the arms of the balance; to the wire or thread used to suspend the plummet (usually reduced to a minimum by the use of a very fine thread); and to the imperfections in the balance (often large in those commonly in use). Many of these errors may be neglected in ordinary work, for instance, those due to cohesion, unless the fluid is very viscous; to difference between true weight and apparent weight in air, if the substance has a density near 1; to the condensed film of air; to the use of a wire or thread; and to the expansion of the arms. It is in the construction that the Westphal balance chiefly errs, one error having been pointed out by Allen (*ANALYST*, 1889, p. 11) in the length of the intervals between the divisions. The beam of the Westphal balance is usually made 10 centimetres in length, so that to insure absolute accuracy the intervals should be 1 centimetre apart, within  $\frac{1}{100}$  of a millimetre, an amount of accuracy which it is not easy to attain in practice, and which may easily be diminished by wear. Another error is introduced in the hook riding on a knife edge, from which the plummet hangs; if the position of this is changed, as it must necessarily often be, a difference in the reading may be observed, amounting sometimes to '001. Another error may occur from one of the riders not sitting absolutely exactly in its place, but inclined to one end of the beam or the other; this error may amount to as much as '0005. The error introduced by the expansion of the plummet is of course obvious, and should be allowed for by noticing the difference between the actual density of water at various temperatures and the indicated density. Unless this is done, determinations made at higher temperatures are only relative, and cannot even be compared with those obtained by another instrument, unless the coefficient of expansion of the material of which the two plummets are made is the same. An inconvenience is felt if the density of a liquid is to be taken at a temperature differing from the temperature at which it is a comparatively large bulk of liquid having to be warmed or cooled as the case may be. I should fix the limit of accuracy of the Westphal balance at not much less than '0005, although closer duplicate readings are often obtained.

The torsion balance is open to all the faults of the Westphal balance, except those due to construction, and besides has the tendency to acquire a slight permanent set, and is not to be recommended except for rough density determinations.

3. Instruments in which the mass of known volume is taken, or pyknometers.—These are practically two in number, the specific gravity bottle and the Sprengel tube and its modifications, neither of which presents any real advantage over the other. It is perhaps rather easier to adjust the temperature of the liquid in the Sprengel tube, but, on the other hand, the Sprengel tube is more liable to lose weight than the bottle, when in constant use. The errors, all of which can be readily allowed for, are the following: those introduced by the condensed film of air, both inside and outside; by the difference between true weight and apparent weight in air; and by the expansion of the glass or other material of which the instrument is made. The most difficult to allow for is the condensed film of air, which I consequently try to eliminate as far as possible by the following plan: dry the bottle or tube by heating it and passing a

current of dry air through it (of course removing the thermometer if the temperature is higher than the highest it will bear), cool, by pouring a current of cold water on the outside, wipe dry and weigh at once; duplicate weighings very rarely differ by as much as .0005 grm. I then fill with distilled water freshly boiled in a platinum vessel, adjust the temperature accurately to 4° C., wipe dry and weigh at once. The increase of weight in grams, corrected for the volume of displaced air, will give the number of cubic centimetres the bottle or tube will hold. The difference between duplicate weighings should not exceed .0005 grm.; the difference between the capacity at 4° and the weight (corrected) of water in grms. held by the bottle or tube at any other temperature, divided by the density of water at that temperature, will give the increase of capacity due to expansion of the glass or other material of which the bottle or tube is made. A table of capacities at various temperatures, and a formula for the expansion, may easily be made of it for each instrument.

TABLE OF DENSITIES OF WATER.  
(Compiled from the results of Pierre, Despretz, and Kopp.)

| Temp. C.        |    |    | Density. | Temp. C. |    |    | Density. |
|-----------------|----|----|----------|----------|----|----|----------|
| 0°              | .. | .. | .99988   | 40°      | .. | .. | .99237   |
| 4°              | .. | .. | 1.00000  | 50°      | .. | .. | .98817   |
| 10°             | .. | .. | .99975   | 60°      | .. | .. | .98343   |
| 15.5° (60° F.)  | .. | .. | .99910   | 70°      | .. | .. | .97794   |
| 20°             | .. | .. | .99826   | 80°      | .. | .. | .97193   |
| 30°             | .. | .. | .99575   | 90°      | .. | .. | .96561   |
| 37.8° (100° F.) | .. | .. | .99313   | 100°     | .. | .. | .95865   |

Should the capacity of the instrument be required at 100° C., some rather special precautions must be taken; the tube should be filled hot, and while the water is absolutely boiling, and the liquid should be adjusted to the proper level, while under slight pressure. I accomplish this as follows (with a Sprengel tube): To the end of the tube from which the liquid is drawn, a tube, about 1.2 c.m. in diameter, having its other end narrowed, and to which a side tube is attached, is fixed by means of a cork; a rod, on the end of which a bundle of filter paper or other absorbent material is fixed, is passed through the narrowed end in such a way that the joint is air-tight (*i.e.* either through a cork or india-rubber); the side tube, and the other end of the Sprengel tube are attached to a bottle, by means of a T-piece, in which a pressure of about ten inches of mercury is kept up by suitable means; the Sprengel tube is, after being filled, immersed in steam, and when the water ceases to expand the rod supporting the filter-paper, is brought to the end of the tube and by its means the water is accurately adjusted to the mark; the tube is then taken out and weighed in the usual manner.

The determination of densities at higher temperatures than 15.5° is usually only required for body that are solid at that temperature, such as butter, and other fats; Muter proposed to do this at 100° F. (37.8° C.) and graduated his instruments with water at the same temperature, and gave to these determinations the name of "actual density," an unfortunate name, as they were really the actual densities divided by the density of water at that temperature. These, however, were good determinations, as there could be no mistake as to what they really were. Three years ago Estcourt proposed to take density of fats at 100° C. by the Westphal balance, a plan which has become rather general among English analysts, but is a distinct falling off from Muter's method, because the expansion, which is not usually allowed for, is enormously increased

at that temperature; and moreover the temperature is exceedingly difficult to obtain, as the boiling point of water depends on the pressure of the air. I do not consider that the results obtained by two analysts taking their densities thus are comparable within  $\cdot 002$ ; the only advantage which this method has over the other, is that beeswax and carnauba-wax are liquid at  $100^{\circ}\text{C.}$  while solid at  $100^{\circ}\text{F.}$  In the regulations for analysis for the State of Colorado, it is laid down the densities of fats shall be taken at  $40^{\circ}\text{C.}$ , which seems to me the most convenient temperature, now that the Centigrade scale is in general use, and I think that we may expect, if the precautions I have drawn attention to are taken, that two analysts should not differ by more than  $\cdot 0002$  or  $\cdot 0003$ .

There are two minor precautions I should wish to draw the attention of analysts to, first, to allow a sufficient time (when using the bottle or tube), for the liquid to contract to its full amount; alcohol contracts very quickly, glycerol very much more slowly, while as an extreme case Perkin has recorded a mixture of aldehyde and water  $\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O}$  which took several hours (*J. Chem. Soc.* 1887, p. 817); the other precaution is to use an accurate thermometer, the great majority of low-priced thermometers being sensibly wrong.

In conclusion, I would recommend that all densities should be the weight (mass) of the substance in the cubic centimetre, that the density of liquids should be taken at  $15^{\circ}$ , and of fats at  $40^{\circ}$ . A symbol, such as  $D_{15^{\circ}}$  meaning density at  $15^{\circ}$  and  $D_{40^{\circ}}$  at  $40^{\circ}$  might be advantageously adopted.

Some results actually obtained are appended.

I. Experiments showing the unequal expansion of specific gravity bottles and tubes:—

| Vol.      | Between $15.5$ and $37.8$ | Expansion per c.c. of capacity. |
|-----------|---------------------------|---------------------------------|
| 25 c.c.   |                           | $\cdot 00042$                   |
| 12.1 c.c. |                           | $\cdot 00055$                   |
| 7.9 c.c.  |                           | $\cdot 00044$                   |
| 5.9 c.c.  |                           | $\cdot 00081$                   |

II. Results obtained in graduating a Sprengel tube:—

|  |                  |
|--|------------------|
| Wt. of Sprengel after heating and rapid cooling        | 18 6308 gr.      |
| " " after standing 15 min. . .                         | 18 6328 gr.      |
| Difference due to condensed air film . .               | $\cdot 0020$ gr. |
| Wt. of Sprengel filled with water at $4.0^{\circ}$ . . | { 30.7622 gr.    |
|  | { 30.7616 gr.    |
| " " " " $15.5^{\circ}$ . .                             | { 30.7523 gr.    |
|  | { 30.7525 gr.    |
| " " " " $30.0^{\circ}$ . .                             | { 30.7158 gr.    |
|  | { 30.7162 gr.    |
| " " " " $37.8^{\circ}$ . .                             | { 30.6865 gr.    |
|  | { 30.6875 gr.    |

Capacity of Sprengel:—

|                | Fund.        | Calc.   |
|----------------|--------------|---------|
| $4^{\circ}$    | 12.1448 c.c. | —       |
| $10^{\circ}$   | 12.1454 c.c. | 12.1454 |
| $15.5^{\circ}$ | 12.1462 c.c. | 12.1462 |
| $20^{\circ}$   | 12.1476 c.c. | 12.1475 |
| $30^{\circ}$   | 12.1505 c.c. | 12.1506 |
| $37.8^{\circ}$ | 12.1535 c.c. | 12.1533 |
| $40^{\circ}$   | —            | 12.1541 |

Formula for capacity at  $t^{\circ}$ :—

$$V = 12.1448 + \cdot 0001(t - 4)^{\circ} + \cdot 0000045(t - 4)^2$$

## ON THE COMPOSITION OF MILK AND MILK PRODUCTS.

BY DR. P. VIETH.

*(Read at Meeting February, 1889.)*

WHAT I have to bring before you to-night is my annual report on the work done during the year 1888 in the laboratory, which is under my charge. Particulars with regard to the purpose for, and the way in which the work is carried out may be found in my former papers of a similar nature (see the ANALYST, VII., p. 53; VIII., p. 33; IX., p. 56; X., p. 67; XI., p. 66; XII., p. 39; and XIII., p. 46), and need not be repeated on the present occasion.

The total number of samples submitted to analysis during the year 1888 is 20,248, comprising—

|        |   |
|--------|---|
| 18,354 | samples of milk.                                |
| 1,144  | „ „ cream.                                      |
| 553    | „ „ skim milk.                                  |
| 26     | „ „ buttermilk.                                 |
| 44     | „ „ butter and butter-fat.                      |
| 6      | „ „ cheese.                                     |
| 35     | „ „ milk preparations for infants and invalids. |
| 59     | „ „ water.                                      |
| 27     | „ „ sundry articles.                            |

In addition to these analyses, the specific gravity of about 75,000 samples of whole and skim milk was determined.

Of the milk samples 12,682 were taken from the railway churns on their arrival in the dairy, and 2,545 by the inspectors employed by the business, from the men while the latter were serving the customers. The following table contains the monthly averages of the results referring to these samples:—

AVERAGE COMPOSITION OF MILK.

| 1888.          | Samples Taken     |               |      |                 |               |
|----------------|-------------------|---------------|------|-----------------|---------------|
|                | On Arrival.       |               |      |                 | On Delivery.  |
|                | Specific Gravity. | Total Solids. | Fat. | Solids not Fat. | Total Solids. |
| January ..     | 1·0325            | 12·97         | 3·79 | 9·18            | 13·0          |
| February ..    | 1·0325            | 13·00         | 3·81 | 9·19            | 13·0          |
| March ..       | 1·0325            | 12·90         | 3·73 | 9·17            | 12·9          |
| April ..       | 1·0324            | 12·81         | 3·68 | 9·13            | 12·9          |
| May ..         | 1·0324            | 12·82         | 3·69 | 9·13            | 12·9          |
| June ..        | 1·0324            | 12·83         | 3·69 | 9·14            | 12·9          |
| July ..        | 1·0320            | 12·82         | 3·76 | 9·06            | 12·9          |
| August ..      | 1·0319            | 12·84         | 3·80 | 9·04            | 12·8          |
| September ..   | 1·0322            | 13·06         | 3·94 | 9·12            | 13·0          |
| October ..     | 1·0325            | 13·09         | 3·89 | 9·20            | 13·0          |
| November ..    | 1·0322            | 13·18         | 4·03 | 9·15            | 13·1          |
| December ..    | 1·0321            | 13·01         | 3·91 | 9·10            | 12·9          |
| Yearly average | 1·0323            | 12·94         | 3·81 | 9·13            | 12·9          |

I may safely leave it to you to draw your own conclusion from these figures.

A further number of 1,806 milk samples was analysed in connection with a very extended investigation into the composition of milk yielded by individual cows kept at

the Aylesbury Dairy Company's estate, near Horsham. The results of this interesting investigation, which was commenced in the year 1887, will form very valuable material, which I hope to be able to lay before you on some future occasion.

As in the case of milk, so in the case of cream, supplied to customers, two series of samples were examined, viz., 412 samples taken before the cream was sent out, and 304 samples taken by the inspectors from the men when working their rounds. The results were as follows :—

AVERAGE AMOUNT OF FAT IN CREAM.

| 1888.                  | Samples Taken    |              |
|------------------------|------------------|--------------|
|                        | Before Sent out. | On Delivery. |
| January .. .. .        | 43·8             | 44·7         |
| February .. .. .       | 43·4             | 43·5         |
| March .. .. .          | 41·1             | 44·4         |
| April .. .. .          | 45·0             | 45·1         |
| May .. .. .            | 45·5             | 46·5         |
| June .. .. .           | 45·1             | 45·9         |
| July .. .. .           | 45·6             | 45·7         |
| August .. .. .         | 45·1             | 46·0         |
| September .. .. .      | 45·6             | 45·5         |
| October .. .. .        | 46·6             | 46·7         |
| November .. .. .       | 48·0             | 48·0         |
| December .. .. .       | 47·2             | 46·6         |
| Yearly average .. .. . | 45·4             | 45·7         |

The agreement between the two series of samples is satisfactory, considering the difficulty of drawing a fair average sample of cream of such richness, and further considering that cream sent out with the morning delivery was sampled before sent out, but not on delivery, being handed to the men, and by the latter to the customers, in sealed cans.

The composition of 55 samples of clotted cream was as follows :—

|                        |                |               |           |
|------------------------|----------------|---------------|-----------|
| Water .. .. .          | 31·57 to 44·11 | average 35·54 | per cent. |
| Fat .. .. .            | 45·78 „ 61·49  | „ 57·09       | „         |
| Solids-not-fat .. .. . | 5·82 „ 10·14   | „ 7·37        | „         |
| Ash .. .. .            | ·44 „ ·80      | „ ·57         | „         |

Skim milk produced by abstracting cream from milk by means of the centrifugal cream separator was exceedingly poor in fat, containing generally less than ·3, and only in exceptional cases more than ·4 per cent. of fat.

The butter samples were derived from three different sources ; six referred to butter churned in the Aylesbury Dairy Company's dairy, fourteen to French, and fifteen to Danish and Swedish butter. I think it will be more instructive to give the results of the analyses of the three kinds separate.

BUTTER CHURNED IN LONDON.

|                               |                |               |           |
|-------------------------------|----------------|---------------|-----------|
| Water .. .. .                 | 10·94 to 12·61 | average 11·72 | per cent. |
| Fat .. .. .                   | 85·66 „ 87·59  | „ 86·53       | „         |
| Proteids, etc. .. .. .        | ·14 „ ·73      | „ ·41         | „         |
| Ash .. .. .                   | ·79 „ 2·51     | „ 1·34        | „         |
| Chlorides, as NaCl .. .. .    | ·68 „ 2·30     | „ 1·20        | „         |
| Insoluble fatty acids, Hehner | 88·27 „ 88·39  | „ 88·32       | „         |
| Deci-normal alkali, Reichert  | 12·9 „ 13·3    | „ 13·1        | c.c.      |

| FRENCH BUTTER, FRESH.            |    |    |                |                         |
|----------------------------------|----|----|----------------|-------------------------|
| Water                            | .. | .. | 13.40 to 14.41 | average 13.79 per cent. |
| Fat                              | .. | .. | 83.98 „ 85.58  | „ 84.86                 |
| Proteids, etc.                   | .. | .. | .89 „ 1.56     | „ 1.16                  |
| Ash                              | .. | .. | .14 „ .25      | „ .19                   |
| Chlorides, as NaCl               | .. | .. | .05 „ .12      | „ .08                   |
| Insoluble fatty acids, Hehner    | .. | .. | 87.15 „ 87.55  | „ 87.38                 |
| Deci-normal alkali, Wollny       | .. | .. | 26.1 „ 27.6    | „ 26.9 c.c.             |
| DANISH AND SWEDISH BUTTER, SALT. |    |    |                |                         |
| Water                            | .. | .. | 11.78 to 15.65 | average 13.72 per cent. |
| Fat                              | .. | .. | 81.72 „ 85.49  | „ 83.11                 |
| Proteids, etc.                   | .. | .. | .71 „ 1.71     | „ 1.09 „                |
| Ash                              | .. | .. | 1.32 „ 2.71    | „ 2.08 „                |
| Chlorides, as NaCl               | .. | .. | 1.12 „ 2.44    | „ 1.85 „                |
| Insoluble fatty acids, Hehner    | .. | .. | 87.30 „ 88.43  | „ 87.78 „               |
| Deci-normal alkali, Reichert     | .. | .. | 13.0 „ 14.2    | „ 13.6 c.c.             |
| Wollny                           | .. | .. | 27.6 „ 29.3    | „ 28.3 „                |

Two samples of butter-fat, which had become bleached by three years' exposure to the action of air and light, contained 83.79 and 84.18 per cent. of insoluble fatty acids respectively.

The examination of two preparations, sold as preservatives for milk and cream under the names of "Preservitas" and "Noigeino" respectively, revealed the old story, viz., that the preparations contained boracic acid as active principle.

In addition to bringing under your notice the above analytical results, I should like to make a few observations on specific gravity determinations.

Although the specific gravity offers such a ready means for the detection of that wholesale adulteration which consists in the addition of large quantities of water, and which has so frequently been, and still too often is, heard of through the police courts' proceedings, it is only of comparatively recent date that attention is paid in this country to the determination of the specific gravity of milk. Of late, however, this determination has become of particular importance, forming, as it does, in conjunction with the determination of the total solids, the basis for calculating the fat, thereby avoiding, or at any rate checking, the determination of the latter constituent.

To ascertain the specific gravity quite correctly becomes under these circumstances of great importance. I am convinced that specific gravity bottle, Sprengel tube, or lactometer give, if carefully used, equally satisfactory results, the last-named instrument undoubtedly with the least amount of trouble. That due regard must be paid to the temperature is a matter of course, but another precaution may be mentioned in this place, which, although it has been long, is still less widely known. I refer to the rise of the specific gravity which takes place and continues for a considerable time in milk, after the latter has been drawn from the udder, and which is quite independent from the escape of gases the milk might have contained.

I availed myself of an opportunity which presented itself to make some observations on this point. The experiments referred to milk yielded by cows kept in a London shed. The cows were milked between 4 and 5 o'clock in the afternoon, a sample drawn from the mixed yield, and its specific gravity determined at about 5.30 o'clock. The determination was repeated on the following morning, at 9.30. Fifteen samples showed an average specific gravity of 1.0296 directly after milking, and of 1.0309 after sixteen hours, or an average rise equal to .0013. In two instances the rise amounted to .0020, in six to .0015, and in seven to .0010.

According to investigations made by Recknagel, the specific gravity becomes stationary, i.e., normal, after five hours or less, provided the milk is cooled down below 15° C.;



at temperatures above 15° C. the apparent contraction proceeds much more slowly, and goes on for twenty-four hours, and even longer. If milk, after its specific gravity had become stationary, is warmed up to 40° C. the specific gravity will be found to have decreased, and it will take some time before it becomes normal again. Recknagel believes that molecular changes in the state of the casein account for the remarkable phenomenon.

*(Conclusion of the Society's proceedings.)*

## ABNORMAL DANISH BUTTERS: A REPLY TO MR. ESTCOURT.

BY ALFRED H. ALLEN.

THE article by Mr. Estcourt on Abnormal Butters, published in the last number of the ANALYST requires no detailed reply from me, but there are some points which it may be well to explain, lest other readers should have drawn as erroneous deductions as those of Mr. Estcourt. It is to be regretted that Mr. Estcourt did not make his criticism the subject of a paper before the Society of Public Analysts, as the misconceptions into which he has fallen could then have been at once met and explained, and time, space, and trouble saved thereby.

Mr. Estcourt writes of my "apparent wish to show that the specific gravity of B and O are normal." In my paper I distinctly make the statement that the average density of butter fat at 100° C. is .8658 (corrected). The abnormal Danish butters B and O are described (page 10) as having specific gravities of .8639 and .8641 respectively. How, in the face of these figures, Mr. Estcourt can have supposed that I regarded or "wished to show" the specific gravity of these samples to be normal I am unable to understand. The very object of my paper was to show that genuine butter might be physically and chemically abnormal to an extent not generally recognised. Everyone knows that there is a marked difference between the density of beef-fat and that of butter-fat, and this difference will be just as great whether the observations are taken with a faulty instrument or an accurately divided one. Mr. Estcourt himself for years used a Westphal balance the plummet of which was broken, and hence was only capable of yielding arbitrary results, strictly comparable among themselves no doubt, but which were incapable of being published or communicated to other chemists.

Whatever Mr. Estcourt may "fear," I am quite prepared, if need be, to maintain, under cross-examination in the witness-box, that no foreign oily matter *could* possibly have been introduced into either of the Danish milks during the manufacture of the abnormal butters B and O. The produce of each of the 31 cows at B farm was brought as obtained by the milkers, who were fully within view, to a weighing machine, where the yield of each separate cow was observed, and the milk then poured through a fine hair-sieve into a tub. All this was done under my eye. The smallest yield from any one cow at B farm was 1 Danish pound\*, and the largest 10 pounds; the total weight of the milk, 119 pounds, which for 31 cows gives an average of 3.8 pounds of milk per cow. Mr. Estcourt, suggests that we should have run this quantity of 13 gallons of milk through a centrifugal separator, and apparently assumes the existence of a separator in every dairy. There was no separator at B farm, and Mr. Estcourt, with his exceptional experience, should be aware that some of the finest butter, both in England and Denmark, is made without a separator. The leaving of the milk or cream for "ripening" is an essential of the Danish system of butter-making.

Mr. Estcourt considers that it was "dangerous" to leave the milk all night, even

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\* 1 Danish pound = 500 grammes = 1.1 lbs. English.

though it was sealed up. As a public analyst, I have had some experience of sealing, and knowing how the milk was sealed in the case in question, I am able to state positively that it was not tampered with. The seals placed on it by the British Vice-Consul (Mr. McGregor) and myself together rendered such a malpractice *absolutely impossible*.

Mr. Estcourt concedes that the supervision of the milking at the Danish farms "was performed by gentlemen whose honour, intelligence, and high ability in the special professions to which they are devoted cannot be questioned," but on the ground of their entire lack of experience of the new calling they undertook, Mr. Estcourt thinks "grave objection might well be taken." Mr. Estcourt is evidently unaware that two of the gentlemen referred to, Mr. Faber and Mr. Bøggild, have gone through a course of training in dairy-farming amounting to a practical apprenticeship, and Mr. Bøggild, in his capacity of consulting Dairy Chemist to the Royal Agricultural Society of Denmark, actually spends his life in visiting the Danish farms, and giving assistance and advice in the manufacture of dairy-products!

It is quite correct that the whole of the dairy operations were conducted under the unremitting supervision of the whole party, and I added the words, "especially Mr. McGregor and myself," because *we* checked the weighing, set our seals on the milk and the finished products, and took other precautions with the express purpose of preventing any imaginable fraud, and of meeting such criticisms as those of Mr. Estcourt.

It is a curious fact that while Mr. Estcourt suggests that the Danish farmers succeeded in surreptitiously introducing foreign fat under the very noses of the party, regardless of the consequences of their detection in the act, from various other sources I am hearing of samples of butter fully as abnormal in character as B and O. In fact, the more general cry is that our experience was not novel.

I sent Mr. Estcourt somewhat more than 30 grammes of the fat rendered from B butter, and am surprised to learn from his paper (page 56) that this quantity was found by him insufficient for the determination of the specific gravity by the Westphal balance.

It is a fact generally recognised that the result of the distillation of butter fat by Reichert's process, expressed as butyric acid, gives a somewhat lower figure than the soluble acids, expressed as butyric acid. But Mr. Estcourt found his G sample to require, when examined by Reichert's process, an amount of alkali corresponding to 4.16 of butyric acid, while the soluble acids in the same sample are stated as equivalent to 3.53 of butyric acid!

I will not ask Mr. Estcourt to state which of these two figures is erroneous, as I write this chiefly as a personal explanation, and do not intend to discuss the matter further.

## QUANTITATIVE ESTIMATION OF ADULTERANTS IN LARD.

By H. W. WILEY.

THE progress of qualitative analysis has rendered it possible for the skilled analyst at the present time to detect with certainty every commercial adulteration of lard. It is probably true that laboratory adulterations amounting to only 2 or 3 per cent. may escape the quest of the skilled chemist; but when adulterations are made for commercial purposes the amount of adulterant added is always in sufficient quantities to render its qualitative detection easy. For quantitative purposes, however, the matter is not so readily determined. For practical purposes the two adulterants which are used in making compound lards are cotton oil and the stearines derived by pressing partially crystallised lard or tallow. The first of these stearines is usually called prime lard stearine, and the second oleo-stearine. The following methods have been proposed for the quantitative detection of these adulterants.

1. *The amount of insoluble residue obtained upon treating the samples with a mixture of ether and alcohol.*—This method, as was shown in the celebrated trial of McGeoch, Everingham & Co., against Fowler Bros., in Chicago, was wholly unreliable, and it may be dismissed from the category of useful methods.

2. *The specific gravity.*—This method has great value, and may be relied upon to give approximate results.

3. *Absorption of iodine.*—This method would be an excellent one for determining the amount of cotton oil added to a lard, provided that no stearine was present; but the careful addition of cotton oil and stearine will enable the mixer to make a lard whose iodine number is almost identical with that of the pure article.

4. *The rise of temperature which samples undergo when mixed with sulphuric acid.*—This process, devised by Maumené, may give valuable information in regard to the quantity of adulterants added. Unfortunately, however, it is open to the same objection as lies against the iodine method, viz., the rise of temperature with the stearine is much less than that with lard, so that by the addition of stearine and cotton oil a mixture can be made in which the rise of temperature is not very much greater than that produced by lard itself.

5. *Melting point of the samples.*—This method is of but little practical benefit when taken alone. Mixtures of lard and cotton oil do not show a mean melting point as indicated by theory. Cotton oil melts one or two degrees below zero, while pure lard melts at about 40°. A mixture of equal quantities of these two substances shows a theoretical melting point of 20°. Such a mixture, however, will melt only a few degrees below the fusing point of pure lard.

6. *Refractive index.*—I am not aware that the refractive index has been used as a method of quantitatively approximating the amounts of cotton oil and stearine added, and I propose to say a few words in regard to its value in this respect. Fourteen samples of lard, known to be pure hog-grease, examined in my laboratory, gave the following mean data:—

|   |    |    |    |    |    |        |
|---|----|----|----|----|----|--------|
| Refractive index                        | .. | .. | .. | .. | .. | 1.4620 |
| Percentage of iodine absorbed           | .. | .. | .. | .. | .. | 62.48  |
| Specific gravity at 35°                 | .. | .. | .. | .. | .. | .9053  |
| Rise of temperature with sulphuric acid | .. | .. | .. | .. | .. | 41.5°  |
| Melting point                           | .. | .. | .. | .. | .. | 40.7°  |

Eleven samples of steam lards passed by the Chicago Board of Trade gave as a mean the following data:—

|   |    |    |    |    |    |        |
|---|----|----|----|----|----|--------|
| Refractive index                        | .. | .. | .. | .. | .. | 1.4623 |
| Percentage of iodine absorbed           | .. | .. | .. | .. | .. | 62.86  |
| Rise of temperature with sulphuric acid | .. | .. | .. | .. | .. | 39.9°  |
| Specific gravity at 35°                 | .. | .. | .. | .. | .. | .9055  |
| Melting point                           | .. | .. | .. | .. | .. | 37°    |

Thirteen samples of Armour's mixed lards gave the following data:—

|   |    |    |    |    |    |        |
|---|----|----|----|----|----|--------|
| Refractive index                        | .. | .. | .. | .. | .. | 1.4634 |
| Percentage of iodine absorbed           | .. | .. | .. | .. | .. | 63.58  |
| Rise of temperature with sulphuric acid | .. | .. | .. | .. | .. | 46.5°  |
| Specific gravity at 35°                 | .. | .. | .. | .. | .. | .9060  |
| Melting point                           | .. | .. | .. | .. | .. | 40.6°  |

Sixteen samples of Fairbank's mixed lards gave the following data:—

|   |    |    |    |    |    |        |
|---|----|----|----|----|----|--------|
| Refractive index                        | .. | .. | .. | .. | .. | 1.4651 |
| Percentage of iodine absorbed           | .. | .. | .. | .. | .. | 85.31  |
| Rise of temperature with sulphuric acid | .. | .. | .. | .. | .. | 57.9°  |
| Specific gravity at 35°                 | .. | .. | .. | .. | .. | .9095  |
| Melting point                           | .. | .. | .. | .. | .. | 38.1°  |

Sixteen samples of purified cotton oil gave the following data:—

|   |    |    |    |    |    |        |
|---|----|----|----|----|----|--------|
| Refractive index                        | .. | .. | .. | .. | .. | 1.4675 |
| Percentage of iodine absorbed           | .. | .. | .. | .. | .. | 106.84 |
| Rise of temperature with sulphuric acid | .. | .. | .. | .. | .. | 83.7°  |
| Specific gravity at 35°                 | .. | .. | .. | .. | .. | .9115  |

Making use of these data, we reach the following results:—

Determined by the rise of temperature with sulphuric acid, Fairbank's lards contained 32.80 per cent. of cotton oil, and Armour's 11.39 per cent. Calculating from their respective specific gravities, Fairbank's lard contained 45.65 per cent. of cotton oil, and Armour's 7.60 per cent. Determined by the iodine absorption alone, Fairbank's lard contained 52.29 per cent. cotton oil, and Armour's 3.6 per cent. As determined by the refractive index, Fairbank's lard contained 56.36 per cent. cotton oil, and Armour's 25.45 per cent.\* The unknown quantity, however, is the effect which the stearines employed had upon the data given. An oleo-stearine examined in my laboratory had an iodine absorption of 18 per cent.; a prime lard stearine an iodine absorption of 44 per cent. Thus more than twice as much of the oleo-stearine could be used as of the lard stearine without perceptibly influencing the percentage of iodine absorption. The specific gravity of the lard stearine used was about the same as that of the lard, viz., .905; although a larger number of determinations might show a lower specific gravity.

The refractive index of one sample of oleo-stearine calculated at 25° was 1.4646. Before formulating any rule in regard to the matter I readily admit that a much larger number of samples of stearine should be examined, and their refractive indices determined. I think, however, it will appear finally that both the specific gravities of the stearines employed, and the refractive indices will be found not to vary greatly from the numbers for pure lard; the specific gravities being somewhat lower. It is seen by the above result that the approximate quantity of cotton oil in lard, as indicated by the refractive index, is much nearer the true proportion for the Fairbank and Armour samples than that given by any of the other methods employed. For instance, let us suppose that the Fairbank samples were composed of 60 per cent. cotton oil, 20 per cent. pure lard, and 20 per cent. lard stearine; the quantity of iodine absorbed by such a lard would be as follows:—

|   |    |      |                 |
|---|----|------|-----------------|
| 60 × 107                                  | =  | 6420 |                 |
| 20 × 62                                   | =  | 1240 |                 |
| 20 × 44                                   | =  | 880  |                 |
| 100 parts                                 | =  | 8540 |                 |
| Iodine absorption theoretical             | .. | ..   | 85.40 per cent. |
| Actual iodine number obtained by analysis | .. | ..   | 85.31 „         |

Thus from the above theoretical calculation the amount of cotton oil added was 60 per cent., which as indicated by the refractive index was 56.36 per cent., by the specific gravity 45.65 per cent., and by the rise of temperature with sulphuric acid 32.80 per cent.

\* The above numbers are calculated from the mean data for the fourteen samples of pure lard and the sixteen samples of purified cotton oil.

In the case of Armour's lard take the following :—

|                           |    |    |    | Ingredients,<br>Per Cent. |   | Iodine<br>Number. | Total.    |
|---------------------------|----|----|----|---------------------------|---|-------------------|-----------|
| Pure lard                 | .. | .. | .. | 70                        | × | 62                | = 4340    |
| Cotton oil                | .. | .. | .. | 20                        | × | 107               | = 2140    |
| Oleo-stearine             | .. | .. | .. | 10                        | × | 18                | = 180     |
|                           |    |    |    | 100                       |   |                   | = 6660    |
| Theoretical iodine number | .. | .. | .. |                           |   | 66.60             | per cent. |
| Actual iodine number      | .. | .. | .. |                           |   | 63.58             | „         |

Let us suppose again that the compound was made with prime lard stearine, in which case we have the following computation :—

|                           |     |    |    | Ingredients,<br>Per Cent. |   | Iodine<br>Number. | Total.    |
|---------------------------|-----|----|----|---------------------------|---|-------------------|-----------|
| Pure lard                 | ... | .. | .. | 70                        | × | 62                | = 4340    |
| Cotton oil                | ..  | .. | .. | 15                        | × | 107               | = 1605    |
| Lard stearine             | ..  | .. | .. | 15                        | × | 44                | = 660     |
|                           |     |    |    | 100                       |   |                   | = 6605    |
| Theoretical iodine number | ..  | .. | .. |                           |   | 66.05             | per cent. |
| Actual iodine number      | ..  | .. | .. |                           |   | 63.58             | „         |

From the above computations the value of the refractive index in determining approximately the respective quantities of cotton oil and stearine in mixed lards is apparent. It is true that in individual cases the variation might be very much greater than indicated above, but as an expression of the mean result it appears to me that the refractive index is fully as valuable if not more so than the specific gravity in the quantitative determination of mixed lards.

I propose to push this investigation somewhat further by more extensive examinations of the specific gravities and refractive indices of lard, oleo-stearine, prime steam lard, and mixed lards.

The refractive index of pure water at 25° as indicated by the instrument employed (Abbe's large model) was 1.3300. When the index of water at the above temperature is taken at 1.3330, .0030 should be added to the numbers given in the above paper.

## ON SOURCES OF ERROR IN DETERMINATION OF NITROGEN BY SODA-LIME, AND MEANS FOR AVOIDING THEM.

By W. O. ATWATER.

(Continued from page 59.)

From these results, as well as from consideration of what is known of dissociation in general, it is evidently impossible to predicate anything definite regarding the amount of decomposition that would take place at a given temperature in a glass tube containing soda-lime and such a complex mixture of gases as occur in an ordinary combustion. I regret the lack of facilities which prevented determinations of the temperature at which the combustions in these experiments were made; but so far as one can judge from observation, I should say that what I have here designated as "medium heat" or "usual heat," namely, that in which the combustion tube is dull red and the soda-lime yellowish, is about that at which combustions are very commonly made in the laboratories where I am acquainted.

Prehn and Hornberger have reported observations which imply large losses of nitrogen by oxidation in soda-lime combustions. When sugar was burned in the tube to expel the air before the combustion and to sweep out the ammonia afterwards, considerably more ammonia was obtained than where this precaution was omitted, and the apparent oxidation by the air present in the tube at the beginning was greater than that from the air used in the aspiration at the end. But the experiments were made with ammonium salts, and where no sugar was used there was apparently no gas to drive out the air and prevent its oxygen from acting on the ammonia. In ordinary combustion of nitrogenous materials large quantities of gases are produced, and in the experiments I have just described oxalic acid was used, which naturally drove out the air.

On the other hand, numerous analysts find that with proper precautions there is no loss from oxidation. In our work we have taken pains to have the tubes well filled with soda-lime and substance so as to leave only very little open space for air, and to heat the anterior layer of soda-lime before applying the heat to the mixture of soda-lime and substance, thus expelling a large part of the air in advance, and have been careful not to aspirate with air until after putting out the flames, so that the contents of the tube have become somewhat cooled before the air has been admitted. In how far omission of these precautions may explain the apparent oxidation elsewhere observed, I, of course, cannot say. Naturally there would be the less danger of loss the more the air is removed by diluting gases before heating. But considerable experience has left me with the very strong impression that with the precautions I have suggested there need be very little fear of oxidation. This must be especially true where, as in ordinary combustions, large amounts of hydrocarbons are present to combine with the oxygen.

Makris has shown that oxidation may take place, but his experiments were made under conditions especially arranged to insure admixture of air with ammonia at a high temperature.\*

Prehn and Hornberger have also experimented upon the effect of different degrees of heat on the ammonia in determinations with ammonium salts and potassium ferrocyanide. They find, at what they call ordinary heat or dull redness, no considerable indications of dissociation, but on heating to bright redness they found with tubes 35-40 cm. and the anterior layer of soda-lime 15 cm. long, considerable, and with tubes 55-65 cm. and the anterior layer 30-40 cm. still more indication of the dissociation of ammonia. Their results thus agree with those above given, except that they get more dissociation with the high heat in the long than in the short tubes. This they very reasonably explain by the fact that the ammonia in the long tubes had more time to dissociate, from which I infer that the gases were caused to pass more slowly than was the case in our work.

Makris also tested the dissociation of ammonia by passing a slow current of gas through a tube 70 cm. long filled with pieces of soda-lime and heated to bright redness. Analysis of the gases coming from the tube showed a very considerable amount of dissociation. But, as Gruber has observed, the case here was different from that in an ordinary combustion, in that a large amount of ammonia was exposed for a long time to

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\* Ann. Chem. (Liebig) 184, 376.

a high heat and without any considerable amount of diluting gas, whereas in ordinary combustion there is less free space in the tube, and that largely filled with other gases, so that the ammonia is rapidly swept away, and furthermore the diluting gases are largely hydrocarbons which would naturally furnish nascent hydrogen to regenerate dissociated ammonia.

My results above detailed accord very exactly with those of Gruber and of Johnson and Jenkins above cited, who found no indications of loss by dissociation. But it is evident that both the complete transformation of nitrogen into ammonia, and the loss of ammonia, depend largely upon the manipulation. Thus Kissling gets very good results with an anterior layer 35 cm. long, and evident loss of nitrogen when the anterior layer is only from 7 to 10 cm. long, the combustion being carried on slowly.\*

The experiments described by Mr. Ball and myself in a previous article bear upon the questions of dissociation of ammonia and of incomplete ammonification of nitrogen of distillation products. They were made with casein, the conditions being varied so as to allow in some cases very little, and in others considerable opportunity for the ammonia formed to be dissociated. The results, given in detail in the article referred to, are more concisely set forth in Table IV.

(To be continued.)

## REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

ESTIMATION OF GLYCERIN IN THE COMMERCIAL ARTICLE. F. FILSINGER. *Zeitschr. f. Angew. Chemie*, No. 1, 1889.—The acetin process recommended by Benedict and Cantor (see ANALYST, 1888) gives good results with the purer kinds of glycerin, but is unreliable for the titration of samples got from soap leys, as these retain impurities which affect the process. Better results would no doubt be obtained if the impurities were first got rid of, but this would involve dilution, and the process only works with fairly concentrated samples.

L. DE K.

TEST FOR ANTIFEBRIN IN PHENACETIN. M. J. SCHRÖDER. *Nederl. Tydschr. v. Pharmacie*, etc. January, 1889.—Phenacetin, when taken internally, yields phenetidin and para amido phenol, both harmless bodies, whilst antifebrin yields aniline, which is decidedly poisonous. It is therefore of importance to test for the presence of antifebrin in phenacetin. The author found the best test to be Plugge's reagent, which consists of a solution of mercurous nitrate with a little nitrous acid. 5 grm. of the sample is boiled in a test-tube with 8 c.c. of water, allowed to cool, and filtered off from the re-crystallized phenacetin. The filtrate is boiled with a little potassium nitrite and dilute nitric acid, then mixed with some of Plugge's reagent, and again boiled. If no red colour is got, the sample may be considered as practically pure; at all events, there cannot be more than 2 per cent. of antifebrin.

L. DE K.

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\* *Ztschr. anal. Chem.* 24, 1885, 448.

**ZINC SALICYLATE.** L. VAN ITALLIE. *Nederl. Tydschr. v. Pharmacie*, etc February, 1889.—The author tests the salt by incinerating the compound, moistening the ash with nitric acid, and finally igniting the residue, which should be not less than 21 per cent. A commercial sample only yielded 18 per cent. The author estimated the degree of solubility of this salt in various fluids. One part dissolves in 25·2 parts of water at 16° C. One part of the anhydrous salt dissolves in 36 parts of ether of 725 sp. gr. at 16° C., and in 450 parts of chloroform of 1·495 sp. gr. at 15° C. One part of the salt dissolves in 3·5 parts of spirits of wine, sp. gr. 819·4 at 15° C. In petroleum spirit it is quite insoluble.

L. DE K.

**MODIFICATION OF KJELDAHL'S NITROGEN PROCESS.** J. W. GUNNING. *Nederl. Tydschr. v. Pharmacie*, etc., February, 1889.—The author operates as follows: One part of potassium sulphate is fused with two parts of sulphuric acid. This mixture gets semi-solid in the cold, but it readily melts, and may then be treated like a fluid. About one gramme of the substance to be analysed is put into a 300 c.c. flask with round bottom and short neck. If liquids such as milk or beer have to be tested, a suitable quantity must first be evaporated to dryness in the flask itself. About 30 c.c. of the acid mixture are now added, and the whole heated with a Bunsen burner. At first strong frothing occurs and white fumes escape, consisting chiefly of water vapour. To prevent loss of strong acid, the neck of the flask is now fitted with a funnel, which is then covered with a watch-glass. This simple arrangement will now cause the acid to condense and run back into the flask. The operation is finished when the acid looks colourless, which will be generally the case after about an hour. After cooling, the ammonia is now estimated as usual. The author prefers the standardising of the volumetric acid by the iodine and sodium hyposulphite method. The test analyses are very satisfactory. Uric acid yielded 33·3 per cent. of nitrogen, theory requiring 33·33 per cent. Aniline oxalate yielded 10 per cent., theory requiring 10·1 per cent.

L. DE K.

**ASSAY OF CARBOLIC ACID.** L. DE KONINGH. *Zeitschr f. angew Chemie*, No. 5.—The author, in reply to Mr. Williams, still believes the salt test to be a good one, both for the liquefied acid of the B.P. and hydrated cresylic acid. If the acid contains much tar oil, it cannot be in the hydrated state, but a little uncombined water may be shown by the benzol test, which, however, is not meant to be used for the purer forms of the acid. The percentage of tar oils is best estimated by agitating the sample with four times its volume of 10 per cent. soda ley if necessary, with addition of a fixed quantity of benzol. Williams' process for the estimation of free acid in carbolic powders is no doubt a most excellent one, but the author fails to see in what essential particular it differs from the one published in the ANALYST, vol. xii., by Dr. Muter and himself. To all intents and purposes it is just the same, though perhaps not quite so accurate, because not performed in specially constructed apparatus.

W. H. D.

**STANDARDISING PERMANGANATE.** R. JAHODE. *Zeitschr f. angew Chemie*, No. 4, 89.—Many analysts still prefer to standardise their permanganate with pianoforte wire, but the trouble always is to exclude the air after the iron has dissolved. The author operates as follows: The iron is dissolved in boiling acid in a flask, which is closed by a cork,



through which goes a doubly-bent tube, the end of which is made to dip into a beaker containing a solution of sodium bicarbonate. When solution is complete and the liquid allowed to cool, the soda solution finds its way into the flask, but no sooner have a few drops got in, than an evolution of carbonic acid gas setting in drives the fluid back.

L. DE K.

### CORRESPONDENCE.

[*The Editor is not in any way responsible for opinions expressed by his correspondents.*]

*To the Editor of the ANALYST.*

SIR,—In the number of the ANALYST for February last, there is a report of a paper by Mr. Rowland Williams on the "Determination of Citric Acid in Lemon Juice," brought before the Society of Public Analysts, "to promote," as Mr. Williams said, "a discussion among the members." I should have been glad to have taken part in such a discussion, had there been one, if Mr. Williams had, in pursuance of his object, kindly informed me that his paper was to be read, and that the greater part of it had reference to what he interpreted as being my method of "Estimating Citric Acid in Concentrated Lemon Juice," and in condemning the use of a solution of an alkaline carbonate for the titration. If Mr. Williams had informed me some months ago, when he asked for some information, that my very general reply was to form the foundation of a paper to be read before the Society, I might have described to him the precautions necessary to be observed in sufficient detail to have saved him from being misled into the belief that there is any objection to the use of alkaline carbonate for the purpose, or of running the risk of misleading others, beyond a little more time being required for the experiment than is necessary when caustic alkali is employed. There is absolutely no inaccuracy involved in use of alkaline carbonate, with litmus as an indicator, when the proper conditions are appreciated and observed.

I have no kind of intention of taking up the space of the journal with a criticism of Mr. Williams' paper as a whole, but I cannot help expressing my surprise at the figures given in the two tables which accompany it.

In the first of these are given comparative results of the analyses of six samples by the caustic method and by alkaline carbonate, showing, according to Mr. Williams, that the carbonate gives uniformly and exactly one ounce of citric acid more in a gallon than the caustic solution.

The only possible explanation of there being difference at all, is that there was interference by carbonic acid retained in the solution; but if Mr. Williams allowed carbonic acid to remain during the final testing, how is it there is anything like agreement in the results and that the differences are almost constant?

In the second table the results of the analyses of seven samples of pure citric acid by the two solutions are given, and the same astonishingly uniform differences are shown.

I cannot think Mr. Williams means to suggest that the alkali in an alkaline carbonate has less saturating power for citric acid than it has as it exists in the caustic condition, and yet this seems to be the only possible inference to be drawn from the tables themselves. My explanation, of course, is that these differences are really errors of manipulation.

I do not think I should have taken up the space of the journal with this letter if I not lately found that Mr. Williams' paper has been distributed widely in pamphlet form amongst manufacturers and dealers commercially interested in the sale of lemon juice, of whom some, at all events, are not in a position to estimate correctly the value of Mr. Williams' criticism of what he believes to be my method of analysis, but which, in fact, is only his mode of employing it. At the meeting at which the paper was read, there seems to have been no discussion, Mr. Allen only expressing what appears to me, to say the least of it, a very hasty "regret" that "chemists of repute" should adopt an alkaline carbonate with litmus as an indicator for the purpose under discussion. Now, in reply to Mr. Williams and to Mr. Allen, I should have thought it might have been assumed by the Society of Public Analysts that chemists of repute, who had been engaged in a special analysis for five-and-twenty years, had carefully examined and tested every process that had been suggested, and under their sense of responsibility, and as the result of their long experience, had adopted the process, which in their hands gave the most reliable returns under all circumstances. Many hundreds of analyses have been made in my laboratory with caustic and with alkaline carbonate solution side by side, and observing the precautions necessary in each case, I, unlike Mr. Williams, obtain identical results, and I protest as strongly as possible against the inferences to be drawn from Mr. Williams' tables, as being opposed to all my experience. There are reasons why sodium or potassium carbonates are frequently to be preferred. After removal of the carbonic acid with properly prepared litmus paper of the proper tint, there is absolutely no objection to their use. As a matter of fact, I do not think Mr. Williams finds it easy to obtain caustic alkali free from carbonate.—I am, sir, yours truly,

39, Lime Street, London, E.C.,  
26th March, 1889.

G. H. UPTON.

# THE ANALYST.

MAY, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL meeting of the Society was held on the 10th ult. at Burlington House.

The minutes of the previous meeting were read and confirmed.

On the ballot papers being opened, it was announced that the following gentleman had been elected as a member :—Mr. W. J. Dibdin, F.I.C., F.C.S., London.

The PRESIDENT said that it was only fitting he should refer to the recent death of Mons. Chevreul, who was an hon. member of their Society. Some years ago he had sent them a letter wishing the Society every success, and he was sure they would all regret his loss. Mr. Allen also made some remarks in allusion to the same subject.

The following papers were read and discussed :—

“Contributions to the Study of the Action of Water on Lead Pipes,” by A. H. Allen.

“Iodine Absorption of Butter Fat,” by Rowland Williams.

“‘Pure’ Chemicals,” by Bertram Blount.

“Some Experiments on the Soap Test,” by Dr. E. Waller.

The next meeting of the Society will be held at Burlington House on Wednesday the 8th May inst.

## NOTES ON LACTOSE.

By E. W. T. JONES, F.I.C.

(*Read at the Meeting, March 1889.*)

ABOUT twelve months ago I carefully purified some milk-sugar, and subsequently obtained some very nice crystals, which after draining, etc., were finally dried in vacuo over  $H_2SO_4$ . The following notes of the results obtained with them I have every confidence in publishing, and although I do not propose to give all the experiments in detail, the results may be taken as very carefully fixed by repeated experiments.

5 grms. (exactly) of the crystals ( $=4.75$  grms. anhydrous lactose) were put into a *correct* 100 c.c. flask, about 80 c.c. distilled water added, and solution effected by heating

in boiling water for twenty minutes to half an hour. The next day the flask was filled up at 60° F. to exactly 100 c.c. Thus I avoided bi-rotation.

The sp. gr. at 60° F. of such a solution is 1.018.6, hence at this concentration the divisor for sp. gr. above 1,000 to get grms. per 100 c.c. of

$$\begin{array}{rcl} \text{C}_{12}\text{H}_{22}\text{O}_{11} & \text{is} & 3.91 \\ \text{and } \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{OH}_2 & \text{is} & 3.72 \end{array}$$

Using a Soleil-Ventzke-Scheibler polariscope, I find at this concentration the sp. rot. pr. for

$$\begin{array}{rclcl} \text{C}_{12}\text{H}_{22}\text{O}_{11} & = & 60.5[a]_D & = & 54.6[a]_D \\ \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{OH}_2 & = & 57.5 \text{ ,,} & = & 51.9 \text{ ,,} \end{array}$$

Cupric reducing power with Fehling solution, using not less than 30 c.c. (diluted with two volumes of water) for 0.1 gm. lactose, heated in vessel surrounded by *boiling water* for fifteen minutes (O'Sullivan's method).

$$\begin{array}{rclcl} \text{CuO} & \times & 0.5723 & = & \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ \text{CuO} & \times & 0.6024 & = & \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{OH}_2 \end{array}$$

I weigh as CuO, *i.e.*, I convert the  $\text{Cu}_2\text{O}$  into CuO by ignition in a porcelain crucible—the whole secret of sure complete oxidation being to use *at first* a *very small* flame to *just char* and destroy the filter paper, after which more heat may be applied and final ignition over the blow-pipe resorted to—proceeding thus the CuO *does not cohere*, and there is not the slightest risk about not obtaining full oxidation by ignition alone—duplicates should not, and generally do not, in my hands, differ more than a milligram.

Action of citric acid.—I have corroborated that lactose is not affected optically, nor in cupric reducing power, by this acid, when proceeding as follows, whilst cane-sugar is completely inverted under such circumstances. Crystallised citric acid is added at the rate of 1.6 grms. per 100 c.c. of solution. Generally I take 50 c.c. of sugar solution and add 0.8 gm. of citric acid, and heat in 100 c.c. flask in boiling water for thirty minutes, and then make up to within half a gm. of the original weight. During the heating a little more loss in volume occurs by evaporation than the increase caused by the citric acid. The weight of the flask, solution and acid being taken before heating, and afterwards made with distilled water to within 1 gm. for 1.6 gm. citric acid, or within half a gramme for 0.8 gm. citric acid, exactly the same volume is obtained after treatment with acid as before, and, therefore, if only lactose is present, the polariscopic readings will be the same.

The proportion of citric acid recommended increases the bulk of the solution  $\frac{1}{100}$ th, *viz.*, 1.6 grms. citric acid to 100 c.c. makes it 101 c.c., and 0.8 gm. to 50 makes it 50.5 c.c., hence we arrive at the proper allowance for adjusting the solution to the original volume.

I have said that cane sugar is completely inverted, and may I be pardoned for mentioning here that although the real sp. rot. pr. of invert sugar is,  $23.75[a]_D$ , *i.e.*, calculated on the increased molecule of the original cane-sugar, if calculated on the cane-sugar, as generally will be the case in practical work, 25.0 must be used.

Crystals of lactose do not lose their water of crystallisation by twenty-four hours' heating in a water oven, but if the crystals be just dissolved in water and evaporated over a water bath to dryness, and then dried in the water oven for a few hours, anhydrous

lactose is obtained ; but the drying must be continued till the weight is constant, which proceeds slowly if the residue is thick. It has been stated that our residues containing lactose after drying in the water oven contain this body in the hydrated state, but this I dispute, if drying is conducted till constant weight occurs.

2.3810 grms. of the crystals after drying for twenty-four hours in the water oven, weighed 2.3806, practically no loss.

0.6828 grm. crystals just dissolved by addition of distilled water, then evaporated to dryness, after drying four or five hours in the water oven, became constant at 0.6500 grm. against 0.6487, the correct amount of anhydrous lactose corresponding to the crystals taken.

It is quite needless for me to point out the practical application of these results in such analyses as those of condensed milk, etc., etc.

#### COLOURING MATTER (ARSENICAL) USED FOR COLOURING CANDLES.

By W. F. LOWE, F.I.C., F.C.S., ASSOCIATE OF THE ROYAL SCHOOL OF MINES.

*(Read at the Meeting, March, 1889.)*

WHILST the use of dangerous mineral colours for colouring tinned and bottled fruits, wall papers, etc., has been pretty nearly stamped out, their use for colouring wax candles appears to have been overlooked. The danger of using them for such a purpose has recently been brought to my notice, and a brief description may be of interest to the members of our Society.

A children's party was given by a gentleman in the district for which I am Public Analyst, and a Christmas-tree with a large number of small coloured candles was the principal attraction. On the day following the party about twenty per cent. of the children who had been present, and also several grown-up persons, suffered from symptoms of irritant poisoning. At first it was naturally supposed that something in the food had caused the mischief ; but on making inquiries the gentleman found that some of those attacked had taken nothing to eat or drink in the house, but had been present at the Christmas-tree, so that it could not possibly be the food. His suspicions then fell on the green candles which had been used for lighting the tree, and as he had had a chemical training, he examined one of the green candles himself, and found traces of arsenic in it. He then forwarded the remainder to me for examination, and I found the green ones contained both copper and arsenic, evidently having been coloured with one of the arsenical greens, which appeared to be "emerald green."

There was not sufficient material to estimate with any accuracy the amount present, but I was able to separate a small quantity of the colouring matter itself by dissolving the wax in warm ether. It is well to note that at first it appears as if the colouring matter had also dissolved, for it is in such a finely divided state that it floats about in the ether for some time, thus giving the appearance of a green solution ; but if it is filtered or allowed to stand a few hours it is seen that it is merely in suspension.

From information I have obtained, it appears to be a common practice in the smaller candle works to use arsenical greens for colouring candles, as they are easier to

use than the aniline green, and stand the action of light so much better, the candles coloured with aniline greens having a tendency to fade unless kept in a dark place.

The quantity employed, I am informed, is from  $\frac{1}{8}$  oz. to over 1 oz. of emerald green to 28 lbs. of wax, and that for the small green candles about 1 oz. to 28 lbs. would be employed. At this rate each small candle, I find, would contain about  $\frac{1}{8}$  grain of colouring matter, and would be capable of yielding about  $\frac{1}{8}$  gr. of arsenious anhydride; so that I should say that a dozen or two of such candles burnt in a room of moderate size would be capable of producing very serious effects.

Red candles also are usually coloured with an injurious mineral colour, at least for such a purpose, for vermilion is used, and a red candle from the same Christmas-tree, I find contains vermilion, but I believe the candles used were chiefly green ones. I intend to make a further examination of the matter, and I hope some of the other members will do the same, for I think that such a practice should, if possible be stopped.

#### DISCUSSION.

Mr. HEBNER said that about twelve years ago he was just about to publish a note on the same subject when he found that Prof. Church had already drawn attention to the matter.

Mr. CASSAL said that the fact of arsenic having been found in candles was not new. Some years ago the question had been brought forward, and it was alleged that some people had been actually poisoned by arsenical candles, but if he recollected rightly they were *white* candles, not coloured ones. The subject was of very considerable interest and importance from a hygienic point of view. The statements that the practice was being stamped out he could not agree with. Most analysts still had a good many things to examine for the presence of arsenic. Some years ago, at the time of the Health Exhibition, he had occasion to examine a number of articles for arsenical and other poisonous pigments, among them butterfly nets, coloured balls, and various children's toys, arsenic in large amount being frequently found. The green gauze used for nets had been found to contain arsenic.

The point was the extreme minuteness of the quantity by which the injury may come about. It would be a good case to help Mr. Dyer, as the whole chain of evidence was complete.

With regard to the use of arsenious acid in candles, he understood it was used to give the burning wick the turn; and if that were so, he was surprised some evil effect had not been discovered.

As to the rash mentioned, that was quite a fact; he had heard of several instances of rash being produced by arsenical pigments, which have an irritating effect on the skin.

The whole matter was very interesting to him from a medical as well as chemical point of view, with the experience he had had.

Mr. ALLEN said that the paper just read showed the desirability of extending the Sale of Food and Drugs Act. Public analysts ought to have under their care all such articles as arsenical wall-papers, fabrics of candles, besides disinfecting powders, &c. The subject was not strictly a novel one, but it was only by calling attention to cases which came within their own experience that it was brought home to them, and he thought they were indebted to the author for bringing the matter forward. He might remind them of the historical case of a member of the royal family of Austria who was practised on by introducing arsenic into the candles used in his bedroom. It was not fair to judge of the poisonous effects of arsenical paper or candles from the amount of arsenic present, for the finely-divided arsenious oxide would be so distributed through the atmosphere as to affect the system far more strongly than if an equal amount had been taken into the stomach; in fact, the effects would probably be more properly

comparable with those attending the breathing of arseniuretted hydrogen, which was known to be intensely poisonous.

He should like to know what became of the copper in the candles. How any candle could contain a measurable or weighable amount of copper which did not go into the wick he could not understand; in fact, if he had had to analyse such a candle, he thought he should have burned the candle and condensed the arsenic by some contrivance similar to that for estimating sulphur in coal gas, and should have looked in the candle end for the whole of the copper which had been previously distributed throughout the candle.

Mr. BERNARD DYER said he would be glad if Mr. Harvey would send him the medical details of the case. It might be known to members that this question of injurious colouring matters, not only applied as to papers, but to other things, had been taken up at various times by various societies, but more especially by the National Health Society. The Society of Arts had previously collected evidence and made a report, but nothing came of it. The National Health Society, in 1883, appointed a committee consisting of medical men and chemists to draft a Bill for the suppression of the sale of arsenical wall paper, on the same lines as the Acts of Parliament in operation on the Continent and, he believed, also in America. In Germany, he believed, arsenical paper was made and exported to this country, but it could not be sold in Germany. In Sweden there was a very stringent law on the subject. The great difficulty in drafting a Bill was in defining the word "arsenical." After considering the question for some time, Mr. Carr, Mr. Heisch, and Dr. Bartlett suggested a very excellent modification of the Marsh apparatus which seemed to meet all difficulties, both as to testing and defining arsenical colours. Dr. Willoughby was at first secretary of the committee, and was succeeded by himself (Mr. Dyer), and the Bill became finally matured during his (Mr. Dyer's) secretaryship, in 1885; and Dr. Cameron undertook to bring the matter before the House of Commons. But the Irish question came up, and Dr. Cameron said it would be perfectly hopeless to bring this forward then, as it would certainly be opposed by the large trade interests, and as he, moreover, was very busy; so nothing was done, and the draft Bill was still on the shelf awaiting an introducer and an opportunity of introduction. The fact remained that England is almost the only civilised country where arsenic-dyed wall papers were allowed to be sold.

One of the great difficulties Dr. Cameron said they would have to contend with was that, as large trade interests were involved, and there would be much opposition, a Select Committee would be doubtless appointed, and that Committee would ask them for their medical evidence. Now, the Society of Arts and the National Health Society had gathered a drawer full of medical evidence, but much of it related to cases where the arsenic was so abundant that, on wiping the paper with a duster, the green came off on the cloth, and much more to cases where patients being out of health, and wall paper being found arsenical, the two facts were assumed to be cause and effect on grounds which, though very strong, did not afford strictly accurate and convincing evidence.

They felt that, before the matter could be brought forward with full confidence, they should strengthen their medical evidence. Any strictly authentic cases of domestic poisoning from arsenic he should be glad to receive on behalf of the National Health Society, that he might hand them to Mr. Kenneth Millican, who had undertaken the collection and collation of medical facts on the question.

Mr. CASSAL said that general practitioners among medical men who had not studied hygiene were not likely to give specially valuable opinions on the points referred to—at least, that was his experience, which was not a small one. Mr. Cassal mentioned the case of a lady who had been wearing a bonnet with bronzed leaves in it, some of these leaves having been kept in close contact with the skin. The leaves contained a large

quantity of arsenic, and the lady had suffered from an obstinate skin eruption and other arsenical symptoms. Another lady who had bought some coloured "Indian" muslin at a large establishment in the West End, and worked at it with her maid, had noticed that both of them were beginning to suffer from inflammation of the eyelids. The muslin was brought to him for analysis, and he found large quantities of arsenic. The vendor had said that he would eat all the arsenic that could be found in it, and he (Mr. Cassal) was sorry he did not do so. The sulphide was at his service.

In another case five or six children were being kept in a room with a large fire in it, the walls being acqwerited with a green arsenical paper. The symptoms had been mistaken for those of a violent common cold.

Dr. MUTER said he had had some similar Indian muslin sent to him, and he also found arsenic in it.

Dr. HARVEY stated that he frequently met with arsenical wall papers. Only on the previous day a case was brought to his notice of serious illness traced to a drab-coloured bedroom paper, which upon analysis was found to contain a considerable amount of arsenic. He was acquainted with numerous other cases where injury appeared to have resulted from the use of such papers.

Mr. ADAMS said that more than twenty times he had had patients suffering from arsenical poisoning. It was a common result that the eyelids became affected; they had a peculiar red appearance which a practical oculist at once knew to be due to arsenic. He had a case quite lately showing what a very minute amount would do the mischief. Of course, in the case of the candles it must have been a very small quantity that each person could have breathed. The poisonous effects of arsenic depended in a measure on two things—first, the idiosyncracies of the person (some could take it with impunity whilst others are injuriously affected by the smallest amount), and secondly, if it gets into the system by the air cells of the lungs it is absorbed much more quickly and injuriously. A lady patient of his had some fur which he had examined and found to contain arsenic. She wrote to him about it on the previous day as follows:—"I am very pleased to tell you anything I can about the fur you found contained arsenic. Directly I began to wear it I had every symptom of a very bad cold in the head, and later on this was accompanied by sore throat and diarrhoea. Naturally in hot rooms I always felt worse" The lady put the fur on one side and at once recovered. When she resumed wearing it, all the symptoms recommenced. This experience was repeated again and again till she came to associate the symptoms with the wearing of the fur, which was then sent to him, and he found out the cause.

## THE METHODS FOR DETERMINING FAT IN MILK.

By DR. P. VIETH, F.C.S., F.I.C.

(*Read at the Meeting, March, 1889.*)

ON looking over the chemical literature of the last decade, we find that much attention has, during that period, been paid to the determination of fat in milk. So numerous are the methods brought out, and the alterations and improvements suggested, that it seems to me, that the supply far exceeds the demand, and that it becomes necessary to classify the various methods in divisions and subdivisions, when attempting to briefly review them in anything like a lucid manner. I will with your permission try to do so in the remarks which I am going to make.

I. Methods which can be worked outside the chemical laboratory, and by persons having no analytical training.

1. Processes confined to the dairy.

(a) *Control apparatus* worked in connection with the Danish Centrifugal Cream Separator. No chemicals required. The milk samples are simply subjected to centrifugal force in suitable vessels, and the volume of cream read off. This volume indicates the percentage of fat sufficiently near for all practical purposes.

(b) *Lactocrite*, worked in connection with Swedish Cream Separator. The milk is treated with strong acids, whereby the fat is, so to speak, set free, and under the influence of centrifugal force unites, so that its volume can be determined. It is generally admitted that results thus obtained agree very closely indeed with those arrived at by determining the fat gravimetrically. At the same time it is rather curious that some experimenters, e.g., W. Blyth, compare it with Adams' method, while others—among them, Soxhlet—compare it with the latter's method; both parties find agreeing results, and still paper and plaster method do not give results agreeing among themselves. It should be mentioned that a smaller machine has been constructed, which can be used in the laboratory of the analyst, although, I am afraid, the price will not facilitate its introduction.

2. *Optical Methods*.—They are based upon the assumption that the opacity of milk stands in direct relation to the amount of fat the milk contains. Not only is this supposition wrong, but the test is also influenced by a number of uncontrollable circumstances. The results are, therefore, always doubtful, frequently quite fallacious. Feser's Lactoscope is, relatively speaking, the best of all the optical tests.

3. *Soxhlet's Areometric Process*.—Milk is mixed with potash solution, and then shaken with ether. The ethereal fat solution is allowed to separate, and its specific gravity determined. A table gives the corresponding percentage of fat. The results may be considered to be identical with those arrived at by extracting milk dried up on plaster of Paris.

4. *Cronander and Liebmann* shake a mixture of milk and potash solution with ether. After complete separation they allow the ether to evaporate and measure the volume of the fat left behind. I do not think these methods recommend themselves, and cannot find that they have been taken up.

5. *Marchand's Lactobutyrometer*.—Milk is shaken in a gauged tube with ether to dissolve the fat; shaking is continued after the addition of alcohol, and the tube then placed in warm water. The mixture separates into three layers; the volume of the upper one, containing the fat, is read off. Every one-tenth c.c. indicates .2 per cent. of fat, in addition to 1.2 per cent. which is kept in solution. The results are fairly correct in the majority of cases, when dealing with milk which is not too rich.

6. *Short* heats milk with strong alkali in a boiling water-bath for two hours, decomposes the soap by the addition of a mixture of sulphuric and acetic acid, allows the liberated fatty acids to rise, and determines their volume, which is then enlarged in the proportion of 87 to 100. This method seems to be rather troublesome, and open to grave objections. The results are said to be lower than those obtained by Adams' method.

II. Methods which must be considered as confined to the chemical laboratory, and the hands of the analyst.



7. *Extracting the fat* from the residue left when milk is evaporated without the addition of an inert substance.

(a) No care is taken to disintegrate the residue (Wanklyn).

(b) Pains are taken that the residue should be in a readily exhaustible condition (Dr. Jas. Bell, Carter Bell).

The difficulty of completely exhausting such milk residues, more especially if the milk is poor in fat, is now generally recognised and the methods may be looked at as abandoned.

8. *Muter* proposes to precipitate the casein which carries down the fat with it; to wash the precipitate first with water, then with alcohol, and at last with ether, which is collected and evaporated, when the fat is left behind.

9. Milk is dried up on some inert substance and then extracted. The substances suggested are glass powder, sea sand, plaster of Paris, asbestos, pumice stone, filter and blotting paper, wood fibre, sponge; and these various modifications are connected with the names of Abraham, Adams, Babcock, Gantter, Johnstone, Macfarlane, Soxhlet, Storch, and others. This group certainly contains the most exact methods for the determination of fat in milk.

10. *Morse* and others suggest to dry milk on anhydrous sulphate of copper, extract the fat by means of light petroleum, saponify, and determine the quantity of alkali required for saponification. I find only one account of experimenting with this method, in which it is said that the results fall below those arrived at by using Adams' method.

11. *Rosse* shakes milk first with alkali, then with a mixture of ether and light petroleum, reads off the volume of the upper layer after complete separation, and determines in an aliquot part of it the fat gravimetrically. An allowance is made for fat retained in the aqueous layer.

12. *W. Schmid* first heats milk with strong hydrochloric acid, after cooling shakes with ether, notes the volume of ethereal layer, and ascertains the fat in an aliquot part. Determining the fat in an aliquot part of its solution appears to me very undesirable, considering that one has to deal with ether, which is not only highly volatile, but the volume of which is also much influenced by temperature; besides, experimental errors are much increased.

This is a rather long list of methods for the determination of fat in milk, and still, I am convinced, it is very incomplete, containing only those methods which have come under my notice and impressed themselves on my memory. Of some of the methods enumerated there exist modifications with regard to the chemicals and apparatus employed.

Very generally acknowledged as standard methods are Adams' paper and Soxhlet's plaster processes; the indications of other methods which do not give direct results are compared with and gauged by either of these processes. Methods like those of *Rosse* and *Schmidt* can claim no other advantage but speed combined with a near approach to correctness. Speed, no doubt, is a valuable item, and approaching correctly results may suffice under certain circumstances, but certainly not with regard to the official work of

a Public Analyst. He ought to employ the most exact methods which are at his disposal.

As an apology for the deficiency of new matter in the foregoing remarks I may say, that they were originally not intended to be read as a separate paper, but meant to be thrown into a discussion which, however, had to be abandoned for want of time.

#### DISCUSSION.

MR. DYER suggested that calcined gypsum might give erroneous results by causing slight saponification of the fat, for gypsum usually contained some carbonate of lime which became caustic on calcination, and might make a lime soap.

DR. MUTER noticed that Dr. Vieth had referred to the method of coagulating the milk with acetic acid, collecting the curd, washing the same first with water and then with spirit, and finally percolating with ether. This was in certain cases a very good way of working as he had had occasion to before mention to the society.

MR. HEHNER said it would be very interesting to get a full catalogue of the different methods. As Dr. Vieth had gone so far perhaps he would go farther and complete it.

DR. VOELCKER corroborated Mr. Dyer, and said that only last week he had such a sample of gypsum sent to him.

MR. ALLEN said that a good many years ago the late Mr. W. W. Stoddart, of Bristol, exhibited what was known as Horsley's process and tube, at a meeting of the British Pharmaceutical Conference, and also described a modified method by which the test was said to be applicable to butter. He, Mr. Allen, was very much interested in the description given, and consequently read a paper on the same subject at the following meeting of the conference, in which he expressed a very unfavourable opinion respecting the method. As a matter of fact, the process did not originate with Horsley, but had been described by Marchand many years previously. The whole subject had gone so completely out of his mind, that when a question was asked him in the "English Mechanic," as to the nature of the lacto-butgrometer, which was simply a Marchand's or Horsley's tube, he said he had never heard of the instrument. Dr. Vieth thereupon pointed out that the instrument had been advertised on the front page of the ANALYST, for a whole year previously, which he was afraid showed that advertisements were apt to be wasted on some people.

DR. VIETH in reply said, that he considered plaster of Paris when employed in milk analysis, an inert substance inasmuch as its desired action was a purely mechanical one. Plaster of Paris was alkaline, but they must remember that milk was not neutral, but displayed besides alkaline, also acid reaction. A number of experiments had shown him that the acidity of milk, was in excess of the alkalinity of the plaster of Paris which he used. He had no difficulty in getting good plaster from Hopkin and Williams.

With regard to the method of extracting the caseine, he had followed that himself in a great many instances, extracting the precipitate after it had been dried in the air bath; he found the results agreed very well indeed with the plaster extraction.

The Marchand's process gave very fair results in the majority of cases, of course, the results were not exact enough for the work of public analysts; but, for instance, in the hand of a farmer who wanted to pick out his best and worst cows, it gave very good results indeed. He had made thousands of determinations; when the fat was within the limits of 3 per cent. and 3.5 per cent. the results agreed very closely. When dealing with richer milks, the results were not so reliable. He would never recommend the process for the use of public analysts, especially at the present day, when the amount of fat could be calculated with great accuracy, from the figures for specific gravity and total solids.

*(Conclusion of the Society's Proceedings.)*

# ON SOURCES OF ERROR IN DETERMINATION OF NITROGEN BY SODA-LIME, AND MEANS FOR AVOIDING THEM.

By W. O. ATWATER.

(Continued from page 76.)

TABLE IV.

*Effects of long heating and of open space in tube upon amounts of nitrogen obtained as ammonia from casein containing 12.43 per cent. of nitrogen.*

| Conditions of Experiments.             | NITROGEN LOST.                    |              |              |                                 |             |             |
|--|-----------------------------------|--------------|--------------|---------------------------------|-------------|-------------|
|  | In per cent. of Weight of Casein. |              |              | In per cent. of Total Nitrogen. |             |             |
|  | Maximum.                          | Minimum.     | Average.     | Maximum.                        | Minimum.    | Average.    |
| No channel, long heating (2½ hours) .. | per ct. 0.47                      | per ct. 0.16 | per ct. 0.35 | per ct. 3.8                     | per ct. 1.3 | per ct. 2.8 |
| Channel, ¾ hour .. .. .                | 1.92                              | 0.05         | 0.65         | 15.4                            | 0.4         | 5.2         |
| Channel, long heating .. .. .          | 2.95                              | 0.00         | 0.68         | 23.7                            | 0.0         | 5.5         |
| Channel, long heating, high heat ..    | ..                                | ..           | 8.51         | ..                              | ..          | 68.5        |
| Channel, long heating, long tube ..    | 9.88                              | 9.29         | 9.58         | 79.5                            | 74.7        | 77.0        |

When the tubes were closely packed so as to insure the maximum of contact between the gases produced and the heated soda-lime (water-vapour at high temperature), and the combustion was conducted at a moderate heat and kept within the usual time of about three quarters of an hour, the full amount of nitrogen, 12.43 per cent. of the water-free casein, was obtained as ammonia. But when the combustion proceeded very slowly so as to occupy two and a half hours, the other conditions remaining the same, only from 12.27 to 12.08 per cent. of nitrogen were obtained as ammonia, making a loss of from 0.16 to 0.47 per cent. reckoned on the weight of the water-free casein, or from 1.3 to 3.8 per cent. of the total nitrogen. It seems reasonable to ascribe this loss to dissociation during the long time that the ammonia was exposed to the heat, though possibly some of it may have been due to incomplete ammonification of nitrogenous decomposition products. It is easy to understand how the ammonia passing rapidly through the interstices between the particles of soda-lime in the closely packed tube, in the ordinary analyses, would be so mixed with water-vapour and other gases that the nitrogenous distillation products would be completely changed to ammonia, and in the very brief exposure to heat the resultant dissociation would be too small to be noticeable. On the other hand, when the operation extends through two and a half hours instead of three quarters of an hour, it would seem by no means improbable that the anterior layer of soda-lime might, before the end of this long period during which it is kept hot, cease to give off any considerable amount of water-vapour. But it is probably this water-vapour which yields the hydrogen to form ammonia with the nitrogen of the volatile distillation products, and it is not impossible that the same vapour may also tend by its presence to prevent dissociation of ammonia. Add the fact that, when the operation goes on slowly, the time of sojourn of the ammonia in the heated tube is of

course relatively much longer than the increased time of combustion would imply, and a large loss by dissociation and incomplete ammonification is easy to understand.

When a channel was left in the tube, so that the contact between distillation products and the soda-lime was less intimate, the loss of nitrogen was still greater. When, with the channel, the combustion occupied only three quarters of an hour, this loss varied from 0.4 per cent. to 15.4 per cent. of the total nitrogen. But when the combustion, with the channel, was prolonged to two and a half hours, the loss reached in one case 27 per cent. of the total nitrogen. This increased loss would seem most probably due to both incomplete ammonification and dissociation. At any rate, the conditions provided for less perfect contact between soda-lime and substance; for reduction of the supply of moisture which would provide hydrogen for ammonification and would also tend to prevent dissociation; and for a very long exposure of ammonia to heat.

When, with channel and long heating as before, the temperature of combustion was raised as high as the tubes would endure, the loss was very much greater, and amounted to 68.5 per cent. of the total nitrogen. The most natural explanation of this increased loss is the increased dissociation of ammonia. When the length of the anterior layer of soda-lime was increased, and with it, consequently, the amount of open space inside the tube, the loss of nitrogen was greater still, namely, from 75 to 79 per cent. of the whole.

It would, of course, be foolish to attempt to say how much of the loss in these latter cases was due to dissociation and how much to incomplete ammonification. Such questions can be answered only by more detailed experiments, in which the gases produced should themselves be analysed. But it does seem reasonably safe to say that both dissociation and incomplete ammonification must account for a large part, if not all, of the errors here observed, and that there is great danger of loss in these ways unless due precautions are observed.

To conclude: As regards loss by dissociation and oxidation, the facts above cited appear to warrant the inferences that, in combustions conducted by the method here described, in which (1) the tubes were so closely packed with soda-lime as to leave a minimum of free space inside, (2) full opportunity was provided for contact between distillation products and soda-lime (water-vapour at high temperature) by the anterior layer of soda-lime 12 cm. long or thereabouts, which was well heated before applying the heat to the mixture of soda-lime and substance, and maintained at a medium heat during the whole operation, and (3) the operation was completed in not over three quarters of an hour:

1. Provided the tube and contents are allowed to cool slightly before aspirating with air, there need be no loss by oxidation.

2. At a temperature sufficient to heat the tube only to dull redness, there need be no considerable loss by dissociation.

3. Ammonia may be dissociated and nitrogen lost by either very high heat, or by conducting the operation so slowly as to leave the ammonia exposed for a long time to heat. Very likely the danger of long exposure is heightened by lack of moisture from the anterior layer of soda-lime after the latter has been heated for some time.

4. A vacant space in the tube (channel as ordinarily recommended) may involve serious loss. This loss is probably due to both incomplete ammonification of distillation products and to dissociation of ammonia.

The danger of loss of ammonia from rapid flow of the gases through the acid solution in the bulb-tube is sometimes assumed to be considerable. Musso, for instance, lays great stress upon uniform and slow evolution of gas, and prolongs the combustion for several hours, the main purpose seeming to be to insure complete absorption of the

ammonia.\* The experiments cited by Mr. Haynes in a previous article imply that the real danger from this source is very small. All his attempts to push the combustion fast enough to force ammonia through the solution were ineffectual. For instance, in a combustion of sulphate of ammonia, completed in 12 minutes, the ammonia, which was sufficient to neutralise half or a little over half of the acid, was entirely absorbed. The volume of the acid solution was 10 c.c.; it was contained partly in the bottom bulb and partly in the outer bulb of an ordinary Knop and Arendt bulb apparatus, in accordance with our usual practice.

*Bearing of the Results upon the Interpretation of those obtained by other Experimenters. The Difficulties with the Soda-lime Method observed by Seegen and Nowack, Musso, and others.*

Of the investigations which have been interpreted as casting doubt upon the reliability of the soda-lime method, those of Seegen and Nowack have, perhaps, been the most frequently quoted. These have carried great weight because the figures obtained were so wide of the truth despite the evident pains taken to secure accurate results, and because similarly bad results have been obtained by other chemists. The apparently unavoidable sources of serious error in the soda-lime method have been alleged as a ground for doubting the correctness of important series of researches in which the soda-lime method has been used. The question of the validity of this doubt is a very important one.

In his account of his own experiments with flesh, Nowack states that care was taken to insure uniform development of gas, and the tubes were kept glowing hot for three hours ("die Röhre stets durch 3 Stunden glühen"). In the report of their joint experiments with animal and vegetable protein compounds, albumin, casein, syntonin, flesh, gluten, legumin, Seegen and Nowack state that they employed the same analytical methods and precautions ("die Analysen wurden in derselben Weise und mit denselben Cautelen ausgeführt, die . . . ausführlich erörtert sind") as were employed by Nowack in his own investigations just referred to. The inference is that their combustions were likewise continued through a long time, if not at a high temperature. Musso, whose experiments were made with milk, whey, and cheese, says his combustions lasted hardly less than three hours, and in some cases they were prolonged for even six hours. In the work of Nowack, of Nowack and Seegen, and of Musso, the figures obtained for nitrogen were very small. Taking those for nitrogen obtained by the absolute method as the standard, the loss of nitrogen in Nowack's experiments reached 20 per cent., and even more, of the whole nitrogen; in those of Seegen and Nowack the loss was from 1 to 20 per cent., while in those of Musso it was over 30 per cent. of the whole nitrogen.

On the other hand, Gruber, who in reply to the criticism of Seegen and Nowack upon analyses by Voit and others in Munich, gives very satisfactory results obtained in Voit's laboratory with protein in flesh, never allowed more than half an hour for the combustions.

The experiments cited by Mr. Woods and myself in article No. IV. of this series seem to us to give satisfactory assurance of the reliability of soda-lime determinations of nitrogen in ordinary protein compounds when the combustions were made with proper precautions. Of the latter, the chief seem to us to be (1) sufficiently fine pulverisation and careful mixture of the substance with soda-lime; (2) close packing of the tube and sufficiently long anterior layer of soda-lime, so as to insure sufficient contact between soda-lime (heated water vapour) and distillation products, as well as to avoid too long sojourn of ammonia in the heated tube; and (3) maintaining the anterior layer at a moderate heat during the whole time of combustion, which should not be too protracted.

\* Ztschr. anal. Chem. 16, 414.

Messrs. Seegen and Nowack do not state whether they left a channel in their tubes or not; but it is evident that the conditions of their work were such as to favour incomplete decomposition of the nitrogenous substance, imperfect ammonification of volatile decomposition products, and dissociation of ammonia. Prof. Seegen reports a nitrogenous residue in the tube after the combustions, and Dr. Nowack found the acid solution in the nitrogen bulbs so highly coloured as to interfere with titration with litmus solution. The combustion was prolonged for three hours, and during part of this time at a very high heat. The determinations of Muss were conducted very slowly, in some cases even more so than those of Seegen and Nowack, and the results obtained were likewise very low. Mr. Ball and I found that either leaving a channel in the tube, or high heating, or prolonging the combustion to two and a half hours, involved large loss of nitrogen, the loss with these conditions combined amounting, in some cases, to two thirds or three fourths of the whole nitrogen.

It would seem, therefore, that we have here cases of a kind not unfrequent in scientific research, in which the very effort to secure correct and reliable results involves grievous error.

I lay especial stress upon this matter because of the use that has been made of Seegen and Nowack's results to discredit the soda-lime method in general, and particularly to throw doubt upon the work of Voit and others in the Physiological Laboratory at Munich, in which this method has been employed in the study of the fundamental problems of nutrition. It was my fortune some time since, while working in that laboratory, to be permitted to observe very closely the ways in which determinations of nitrogen by soda-lime are there conducted. Although the effort to insure close packing of the tubes was perhaps less than in the experiments above detailed, and upon which the conclusions here given are based, yet on the whole the details of manipulation as I observed them were such as would, with the experience in this laboratory, lead one to expect correct results.

Although the results of experiments by Gruber and others in the Munich laboratory, and accumulated experience elsewhere, make any vindication of its work superfluous, yet I trust these statements, in connection with an explanation of the error into which Seegen and Nowack have unwittingly fallen, may, in the interests of science, not seem out of place.

The experience of other chemists, as well as that in this laboratory, of which part has been described in these pages, leaves me with the decided belief that the Scylla and Charybdis of the soda-lime determination are incomplete ammonification of nitrogenous distillation products and dissociation of ammonia. The other difficulties are, in general, easy to overcome. They may all be prevented, in ordinary animal and vegetable protein compounds, by the precautions above enumerated. But in alkaloids and allied compounds, and in some amines, and amido and azo-compounds, loss by incomplete ammonification seems very difficult to avoid.

The observations I have had occasion to make, as well as printed accounts of the methods followed in different laboratories, have given me the decided impression that the most common difficulties are loose packing of the combustion tube so as to leave a channel, insufficient anterior layer of soda-lime, and too high or too long-continued heating.

The soda-lime method is beset with dangers, and requires great care to avoid them. Indeed, after the experience in this laboratory, covering a period of several years and including some thousands of nitrogen determinations, if I were going to undertake again a series of analyses like those for which these studies were made, and the details of the work were to be placed in the hands of an analyst, however expert, who had not been through some such experience as that above described, I should feel under the

necessity of asking him to do a considerable amount of preliminary work, including comparison of results by the soda-lime with other methods, before I could feel sure of his results. A case in point may be worth mentioning.

After most of the above detailed experiments had been made and we had the method in such control that we were wont to say jocosely that from a given protein compound we could obtain the whole or any desired fraction of the nitrogen as ammonia, at will, a gentleman of no little experience, and who afterwards proved himself a skilful and efficient analyst, came to our laboratory as assistant. We placed a number of substances, mostly animal tissues, in his hands for nitrogen determinations by the soda-lime method, instructing him in the details of the process, and going through a number of determinations with him. He was very confident that he could secure perfectly reliable results and at the same time make the determinations with considerable rapidity. After a list of substances had been analysed, I looked over his figures, and was somewhat surprised at the variations in the duplicate determinations, which, in some cases, as I now recall, reached nearly 0.2 per cent. This led me to question their accuracy. Mr. Woods, by whom most of the nitrogen determinations of this investigation have been made, repeated the analyses and found in almost every case a considerably higher percentage of nitrogen, so that the whole work had to be repeated. The most plausible explanation of the errors seemed to be that the determinations in question were made rather hurriedly, and either because the nitrogenous material was not well enough mixed with the soda-lime, or from too loose packing of the tube, some of the nitrogenous distillation products were incompletely ammonified, and thus escaped detection in the titration subsequent to combustion.

At the same time I must repeat what I have already said, that our experience leads me to place the greatest confidence in the soda-lime method for the determination of nitrogen in ordinary protein compounds, provided the work be conducted with the precautions here insisted upon.

The perfection to which Kjeldahl's method has lately been brought, and its accuracy, convenience, and inexpensiveness, have led to its use in this as in many other laboratories. Our experience leads us to decidedly prefer it to the soda-lime method, though we find it advantageous to use both, making one check the other. But the danger of incomplete ammonification of some classes of compounds, *e.g.*, alkaloids, makes us feel it necessary to control both by the absolute method for all classes of substances, except those for which they have been most thoroughly tested.

#### SUMMARY.

The experimental and other considerations presented in this and the previous articles on the determination of nitrogen by soda-lime, may be conveniently summarised, after first recalling the probable reaction by which the nitrogen is changed to ammonia, and the principal sources of error in the operation.

1. It seems decidedly probable that the change of nitrogen to ammonia is effected by union, at high temperature, with water vapour yielded by the soda-lime (or slaked lime in case the latter is used). It is essential that the contact between nitrogenous distillation products and water vapour be sufficient, and not at too high or too low temperature to insure conversion of all the nitrogen to ammonia, and that the ammonia be not dissociated or oxidised. The main objects, then, are to secure complete ammonification and to avoid dissociation and oxidation.

2. The chief difficulty in the way of complete ammonification of protein compounds appears to be the formation of gases which do not readily yield their nitrogen to be united with the hydrogen of the water vapour. With certain other classes of nitrogenous compounds, as leucine and its congeners, alkaloids, amines, and amido and azo-compounds,

this difficulty is greater, and sometimes apparently insuperable. The tendency of protein compounds to be decomposed by heat and other agencies into leucine, amines, etc., appears to explain the difficulty frequently found in getting all their nitrogen into the form of ammonia by heating with soda-lime. The evident means to secure complete ammonification must be sufficient contact with soda-lime at proper temperature.

3. The danger of dissociation of ammonia evidently increases with increase of temperature and time of exposure, and is probably diminished by presence of water vapour and other diluting gases. If this be so, the danger will be avoided by measurably rapid combustion at not too high heat, and by keeping the ammonia in contact with sufficient moisture from the soda-lime until it leaves the heated tube.

4. Leaving out of account substances such as nitrates, nitro-compounds, etc., whose nitrogen is imperfectly converted into ammonia by soda-lime, even in the presence of organic matter, and assuming palpable errors of manipulation, to be avoided, such as (a) loose packing of asbestos plug, which would allow particles of soda-lime to be swept into the acid bulb; (b) heat at anterior end of the tube, so low as to permit ammonia to be retained with moisture about the cork, or so high as to char the cork and give rise to acid or alkaline distillation products; (c) use of soda-lime containing nitrates or nitrites, which may, according to circumstances, either furnish nitrogen to be transformed into ammonia, or oxygen to burn the ammonia formed from the nitrogen of the substance; (d) use of distilled water containing ammonia for rinsing the acid bulb; (e) imperfectly-cleaned or incorrectly-calibrated burettes; the principal sources of error above discussed involve loss of nitrogen, and may be recapitulated thus:

I. Loss from imperfect ammonification of the nitrogenous substance, due to:—

a. Incomplete decomposition of the substance, part of the nitrogen being, from coarseness of the particles of the substance, imperfect mixing with the soda-lime, insufficient heat, or other cause, left behind in the charred residue.

b. Change of nitrogen into compounds other than ammonia, either such as may remain in the tube, *e.g.*, cyanogen; or volatile distillation products which escape ammonification and pass through the acid solution unabsorbed, or, if absorbed, are not accurately determined by the titration or other means used to find the amount of nitrogen in the solution.

c. Escape of nitrogen in the free state.

II. Loss of ammonia through:—

a. Dissociation at high heat in the combustion tube.

b. Oxidation by air present in the tube before, or introduced in aspirating to wash out ammonia after, the combustion.

c. Neutralisation by acid products, *e.g.*, of sugar, where the latter is used in the combustion.

d. Incomplete absorption by the acid solution.

5. Complete decomposition of the substance has, in our experience, been readily secured by pulverisation fine enough for it to pass through a sieve of 1 mm. aperture; thorough mixing with soda-lime; avoiding the shaking by which the particles gather at the top of the soda-lime; and heating to low redness.

6. With sufficient soda-lime, not too dry, we have found no reason to fear the formation of cyanides, nor have we been able to obtain any indication of the escape of free nitrogen when the operation is properly conducted, although it might, perhaps, occur by oxidation of ammonia if there were nitrites or nitrates present, or if aspiration with air were done while the tube and contents are hot. Turning off the flame before aspirating has, in our experience, sufficed to avoid oxidation by air. At least, if ammonia has been oxidised, the quantity has been too small to be detected.



7. When sugar is used, acid products may be formed in quantities large enough to impair the accuracy of the determinations. With ordinary animal and vegetable protein compounds, provided enough soda-lime is employed, the use of hydrogen or sugar, or other substances for supplying gases, either to expel air, or to yield nascent hydrogen to form ammonia with the nitrogen, or to dilute the ammonia and prevent dissociation, or to wash out the ammonia, appears to be unnecessary. The danger of loss by incomplete absorption of the ammonia by the acid solution appears to be very small indeed, even when the development of gases is very rapid, provided sufficient acid solution be used.

*(To be continued.)*

### CORRESPONDENCE.

*[The Editor is not in any way responsible for opinions expressed by his correspondents.]*

*To the Editor of the ANALYST.*

#### ABNORMAL BUTTERS: A REPLY TO MR. ESTCOURT'S PAPER IN "THE ANALYST," MARCH, 1889.

SIR,—Mr. Estcourt appears to have had two objects in view in his paper on "Abnormal Butter," viz.: (1) to show that Mr. Allen failed to prove the existence of genuine butter of an abnormal composition, and (2) to defend the conclusion drawn from his analysis of a sample of butter from Wigan.

As to the first point, Mr. Allen has already answered. So many cases of abnormal butters have been found of late, that had Mr. Allen not brought the subject before the Society, some other analyst would surely have done it by this time.

On the second point, I may explain why at the time I considered the question of the Wigan butter to be one of abnormal butter, but shall at once admit that—as far as Mr. Estcourt is concerned—I was mistaken. Had Mr. Estcourt been more willing to discuss the matter at an earlier stage, the whole case would probably have received quite a different treatment.

Some butter was sampled at Wigan last summer and pronounced to be adulterated. Mr. Estcourt, who analysed the sample for the defendant, certified it to be "a sample of margarine," "having regard both to its specific gravity and the very low per centage of soluble fatty acids." This is the sample No. 402 of Mr. Estcourt's paper.

Some samples of butter were taken at the dairy from which this butter No. 402 was believed to have come. These were marked "G" and "N."

Some of these samples G and N were sent to Mr. Estcourt, who wrote of them, "The specific gravity of both is lower than that of any genuine butter I have yet analysed. The soluble fatty acids are also not present in such a per centage as to indicate a genuine butter." From the figures in his paper on "Abnormal Butters," it appears that he found No. 402, G and N, almost identical in their composition.

Professor Stein found those samples, G and N, to yield about 24 c.c. by the Reichert-Wollny process, and a small sample of butter-fat sent him from the agent of the shipper of the Wigan butter, who had obtained it from Mr. Estcourt as the remainder of sample 402, yielded the same amount of volatile acid, viz., 24 c.c.

The two analysts were therefore agreed upon the very close similarity between these three samples. I shall not enter into any discussion as to the supposed genuine nature of sample G; it is not to the point here. I merely wish to deny ever to have written about "the supervision of the milking" from which samples G and N were

obtained. I only note that both analysts found the Wigan butter and samples G and N very similar; of G and N samples exist still in the original packing and with unbroken seals.

The genuine nature of a butter-fat yielding  $24^{\circ}$  c.c. by R.-W. may well be questioned, as such butter-fat is of rare occurrence, which fact has made Professor Stein name it "abnormal." He did at first question the genuineness of the butter from the dairy in question, but having learnt the history of sample G he—rightly or wrongly—altered his opinion, and pronounced this butter genuine but abnormal, and having found the sample of butter-fat, said to be the remainder of Estcourt's sample 402, to be very similar to sample G, he concluded that abnormal butter of this composition was not known to Mr. Estcourt.\* Having at the time no knowledge of the actual results of Mr. Estcourt's analyses, I concurred in Professor Stein's view, and I concluded that a demonstration of the existence of genuine butter of this composition, taken with sufficient guarantee, would suffice to show that the analysis of the Wigan butter (402) was not sufficient proof of its adulteration. I do not yet see how we could have come to a different conclusion.

My first step was then to write to Mr. Estcourt (on Sept. 18th), asking him for the particulars of his analyses of the samples, mentioning that the Wigan case was "likely to throw some new light on the question of the variations of volatile or soluble acids in butter." Mr. Estcourt replied (Sept. 20th) that he should "be pleased to exchange particulars of analyses" with me, if I would give him the results obtained by the chemist in Denmark. On Sept. 28th I called on Mr. Estcourt in Manchester, and gave him the figures he has published, as obtained by Professor Stein, being all that Professor Stein had at that time estimated in the three samples. I naturally understood that Mr. Estcourt would give me his figures in return; but although I urged him to do so, he declined, promising, however, that he would send them on three days later. *I have never since heard from him.* It is somewhat surprising that he should complain that he "heard no more of this matter," for I left him with the understanding that I was first to hear something from him.

My plan to discuss with Mr. Estcourt the question of the existence of genuine butter yielding 24 c.c. R.-W., had, of course, to be given up after this breach of promise. I therefore sought and obtained the assistance of Mr. Allen.

Had Mr. Estcourt, according to his promise, made both by letter and verbally, informed me that he had found about 3.5 per cent. of soluble fatty acids in these samples, I should then have seen at once that the question was not one of "abnormal butter," but of "abnormal analysis," and I should have proceeded accordingly. It could never enter my mind that a sample of fat containing only 3.5 per cent. of soluble acids could be genuine butter-fat; but neither could I ever be expected to suppose that in a sample yielding about 24 c.c. by R.-W., anybody could find only 3.5 per cent. of soluble acids.

Mr. Estcourt speaks of "the Reichart method." He does not mean that, however. From the way in which he uses the name "Reichart," I gather that he means the Reichert-Wollny method, which is described by Mr. Allen as the one used by him and Professor Stein. Mr. Estcourt argues against this method, that it is liable to give erroneous results, in extreme cases—according to Wollny—30 per cent. *too low*. But he does not mention, although he quotes the very paper by Wollny, that these errors are those of the original process, and that they are impossible when using the method as modified by Wollny! But, even should Mr. Estcourt have employed the original and faulty Reichert's method, how did he succeed in getting a result which is just 30 per cent. *too high*?

\* As stated previously, Professor Stein had met with abnormal butter yielding even less than 24 c.c. the year before this Wigan case.

"I desire to call attention to the paper by Dr. Wollny in the January and February numbers of *THE ANALYST* for 1888," and I ask, how is it possible that an analyst should find 30 per cent. *too high* a result, even if he cares to ignore the improvements to the method? Wollny finds that carbonic acid in the original process may cause an error of +10 per cent. *as a maximum*.

After the publication of Mr. Estcourt's paper, I asked Professor Stein to estimate the soluble fatty acids in samples G and N, and in the remainder of the small sample obtained from Mr. Estcourt as No. 402. With his permission, I publish the results of his analyses, obtained by the modification of the method suggested by Dr. Muter. I give (1) the per cent. of soluble acid; (2) the result by Reichert Wollny; (3) the per cent. of butyric acid corresponding to the number of c.c. of  $\frac{N}{10}$  found by R.-W.; and finally (4) the per cent. of butyric acid found in this way by R.-W., expressed as per cent. of the total amount estimated by Muter's method. To this I add the results of Mr. Allen's analyses of samples B and O, and of Mr. Estcourt's analyses of samples 402, G, N, B, and O, all calculated in the same manner.

|     | p. c. Soluble Acid. | R.-W. c.c. =    | p. c. Butyric Acid = | p. c. of Total Soluble Acids. |
|-----|---------------------|-----------------|----------------------|-------------------------------|
|     |                     | BY PROF. STEIN. |                      |                               |
| 402 | 4.7                 | 24.0            | 4.22                 | 89.8                          |
| G   | 4.70                | 24.2            | 4.26                 | 90.6                          |
| N   | 4.79                | 23.9            | 4.21                 | 87.9                          |
|     |                     | BY ALLEN.       |                      |                               |
| B   | 4.44                | 22.39           | 3.94                 | 88.7                          |
| O   | 4.68                | 24.70           | 4.35                 | 92.9                          |
|     |                     | BY ESTCOURT.    |                      |                               |
| 402 | 3.40                | ..              | ..                   | ..                            |
| G   | 3.53                | 23.60           | 4.15                 | 117.6                         |
| N   | 3.57                | 22.55           | 3.97                 | 111.2                         |
| B   | 4.51                | 22.44           | 3.95                 | 87.6                          |
| O   | 4.70                | 24.64           | 4.34                 | 92.3                          |

The only acid in butter-fat which is volatile, and not soluble, is capric acid, but as it amounts to less than one per cent. of the total amount of soluble acids, it is of no consequence. As only about four-fifths of the solution is distilled off in the Reichert-Wollny process, only part of the volatile acids pass over in the distillate, viz., about 90 per cent. Mr. Estcourt, however, has succeeded in distilling over considerably more than the total amount of the soluble acids! In sample G he found 3.53 per cent. of soluble acids, 90 per cent. hereof is 3.177, which calculated to 5 grams. of fat, and expressed as c.c. of  $\frac{N}{10}$  solution of butyric acid is 18. This figure, therefore, should be the result by R.-W. of a sample of butter containing 3.53 per cent. of soluble acids. Mr. Estcourt found 23.60, or, he found either 30 per cent. *too high* a result by Reichert-Wollny (which beats the record), or he found 1 per cent. *too low* a result by estimating soluble acids, which means that over 20 per cent. of the soluble acid escaped his notice.

As his opinion of the Wigan butter is based on his estimation of the soluble acid, it is therefore not surprising that he should consider it adulterated. I must however necessarily doubt the correctness of his analysis, and thereby his right to conclude, that the Wigan butter was adulterated.

Yours faithfully, HARALD FABER.

*To the Editor of the ANALYST.*

SIR,—I shall only occupy a very small space in reply to Mr. Allen's reply.

I desire to call especial attention to the statement which he boldly makes, (apparently from his own knowledge), that I for years used a Westphal balance of which the plummet was broken, and the results obtained with it which were incapable of being published.

In answer to this, I can only say I am pleased to believe that the most of Mr. Allen's statements have a better foundation on fact than this, or the scientific world would suffer.

Mr. Allen does not give his authority for this incorrect statement, so he must have evolved it from his inner consciousness.

Since 1876, when I first introduced the Westphal balance to chemists in this and other countries, for ascertaining the specific gravity of liquids at high temperatures, I have always had in my possession at least one duplicate bulb made by Westphal, for my instrument, which is also subdivided by Westphal to indicate half degrees.

In November, 1885, I suggested to Mr. Allen that he should give up quoting specific gravities, at 100 F. and use my apparatus and bath, &c.

He thanked me for my suggestion and altered the whole of the gravities in his new volume in accordance with the method which I have been using since 1876.

This much of ancient history I have given in justice to myself, as it will serve probably better than anything else to show the improbability of Mr. Allen's statement.

With regard to Mr. Allen's other statements, they are already sufficiently answered in my paper published in the March number of the ANALYST.

The allusion, in the last two paragraphs, to the Reichert result of G sample serve to show what has been already stated, that the Reichert process gives erratic results.—I am, sir, yours,

CHARLES ESTCOURT.

*To the Editor of the ANALYST.*

SIR,—In connection with the articles on Abnormal Butter which have appeared in recent numbers of the ANALYST, the following lines may be of interest.

In December, 1885, both at the beginning and the end of the month, I made in my Laboratory butter from the milk of a single cow, and this butter, both in my own hands and those of Mr. Shippen Wallace, Chemist, Philadelphia, Pennsylvania, gave by the Reichert test figures ranging from 11.3 to 11.5 c.c. of deci-normal alkali consumed in neutralizing the first acid distillate of 50 c.c. I found the insoluble fatty acids (by Lehner's process) to be 89.6 per cent.

As stated by Wallace and myself (*Ninth Annual Report*, N.J. State Board of Health, 1885), the cow was one of a herd of eight cows in Princeton, N.J. She was of mixed breed, chiefly Alderney; nearly five years old; had a calf about eight months before, and was expected to have another late in the following spring; yielded six to seven quarts of milk daily at that time; her food was barley meal and corn-stalks (maize); she was apparently in sound condition. The butter made separately from five other cows in the same herd, within the same week or nearly so, ranged from 12.2 to 15.1 c.c. deci-normal alkali, so that neither the season of the year nor the food appeared to have any influence on the result.

In consequence of this result, we recommended that the minimum for butters made from the milk of a single cow should not be above 11 c.c. of deci-normal alkali.

I have no doubt that the milk was delivered to me in its normal condition, because I sent my own private messenger to obtain it; the owner of the herd did not know what use was to be made of it; exactly the same result was obtained from the milk at intervals of a month (or within very narrow limits, the same results); and finally, the milk from five other cows in the same herd was normal as to the behaviour of the butter fat.

While this is not intended to have any especial bearing on Mr. Estcourt's paper on Abnormal Butters, ANALYST, March, 1889, it is presented as evidence that pure butter fat from the milk of a single cow, under normal conditions so far as we can judge, may yield by Reichert's method, figures decidedly below the usual standard.

I would add that I place more dependence on Reichert's than on any other process, and do not hesitate to condemn by its results butters which I can know have been made in this country and from the mixed milk of several cows; accepting then as high a standard as 11.5 to 12 c.c. of deci-normal alkali.—Respectfully yours,

John C. Green School of Science,  
Princeton, New Jersey, U.S.A.  
March 20th, 1889,

H. B. CORNWALL.

*To the Editor of the ANALYST.*

**"ON THE DETERMINATION OF CITRIC ACID IN LEMON JUICE."**

SIR,—Will you kindly permit me to make a brief reply to the letter of Mr. G. H. Ogston (not Upton) on the above subject, which appeared on page 86 of the April number of the ANALYST?

Mr. Ogston says he would have been glad to have taken part in the discussion on my paper had there been one, and complains of my not having informed him of my intention to criticise the method which he employs for the examination of lemon juice. This was surely quite unnecessary. Mr. Ogston is a member of the Society of Public Analysts, and would no doubt receive due notice of the title of my paper, so he could presumably have attended the meeting if he desired. I can scarcely be held responsible for Mr. Ogston's absence, and I can assure him that no one anticipated and wished for his presence more than myself. Mr. Ogston is quite mistaken when he insinuates that, some months previously, I wrote asking him for certain information with the object of making it the basis of my paper. My sole reason for communicating with Mr. Ogston was because there had been complaints from calico-printers in this district at the discrepancies which were sometimes found to occur between my figures and Mr. Ogston's, and I thought it would be to our mutual advantage if our results agreed more closely in future. The explanation offered by Mr. Ogston with regard to the cause of the difference between our results, viz., the presence of carbonic acid in my titrations is, though plausible enough, altogether inadequate. I am quite certain that no carbonic acid could have been present, as in all the experiments every possible precaution was taken to ensure accuracy.

I followed Mr. Ogston's own directions as carefully as possible, viz., "Have the test paper nearly neutral and light in colour. After the addition of about two thirds of the necessary quantity of soda solution, boil for ten minutes to expel carbonic acid, and boil between each subsequent addition of the test." There seems to be some uncertainty in Mr. Ogston's mind as to whether I meant to suggest that the alkali in sodium carbonate has a different saturating power for citric acid than the alkali in caustic soda. What I clearly meant, and what I still contend is that, when titrating solutions of citric acid with sodium (or with caustic soda for that matter), using litmus paper as indicator, the point of saturation is reached sooner (owing to the alkaline reaction of sodium citrate to litmus paper) than when caustic soda and phenolphthalein are employed, consequently the sodium carbonate appears stronger than is theoretically possible. For instance, suppose 7 grains of pure citric acid are dissolved in water, and the solution titrated with normal caustic soda, using phenolphthalein as indicator, 100 fluid grains will be required. But if, on the other hand, normal carbonate of soda solution and litmus paper are employed, the addition of, say 97 grains, with subsequent thorough boiling and cooling, will in all probability be sufficient to produce a distinct blue colour; 100 grains of the alkaline solution would, therefore, appear capable of neutralizing 7·2 grains of citric acid, owing to the unsatisfactory nature of the indicator employed. For obvious reasons Mr. Ogston seems to be aggrieved because reprints of my paper have been distributed among those interested in the matter, but I may say that the majority of these persons entirely approve of my action.

While writing, I have before me a letter from the chemist at a well-known calico-printing works, confirming my statement with regard to the greater accuracy of citric acid determinations made with caustic soda and phenolphthalein.

For my own part, I know of no "reasons why sodium and potassium carbonates are frequently to be preferred," as is stated by Mr. Ogston near the close of his letter.

Mr. Ogston may protest as strongly as he pleases against the inferences to be drawn from my tables, but, to slightly alter the words used by Mr. Allen in the discussion which followed my paper, and which Mr. Ogston rather strangely ignores, "there can be no doubt on which side the truth lies,—I remain, sir, yours faithfully,

ROWLAND WILLIAMS.

28, Pall Mall, Manchester,  
April 10th, 1889.

CATALOGUE of Chemical and Physical Apparatus, and Chemicals Manufactured and Imported by Philip Harris and Co., Limited, Bull Ring, Birmingham. This is a very complete and exceedingly well got up catalogue, the illustrations being numerous and well executed. The list of physical apparatus is most complete, and does great credit to the firm.

A TREATISE on Manures; or, the Philosophy of Manuring. A practical handbook for the Agriculturist, Manufacturer and Student, by A. B. Griffiths, Ph.D., F.R.S. (Edin.), F.C.S. London; Whittaker and Co.

ERRATUM. Mr. G. H. Ogston, F.C.S., F.I.C., 39, Lime Street, E.C., was the writer of the letter, which, by a printer's unfortunate error, appeared over the signature, "G. H. Upton," in our last issue.

# THE ANALYST.

JUNE, 1889.

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### PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL meeting was held at Burlington House on the 8th inst., the President, Mr Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

Mr. A. J. Hailes, Analytical Chemist, Hornsey, was proposed as a member.

The PRESIDENT said that the Council would be glad to receive from members before the next meeting (this month) suggestions as to where the usual country meeting should be held; one or two places had been mentioned Liverpool and Paris—but before finally deciding, the Council would like to know the views of members on the question.

The following papers were read and discussed:—

"On the discrimination of the various species of *Saccharomycetes*," by Dr. W. J. Sykes.

"Fat Extraction from Milk Solids," by H. D. Richmond.

The papers announced by Mr. Faber and Dr. Vieth were, owing to the lateness of the hour, postponed until the next meeting.

In the course of the evening the President, at the suggestion of Mr. Cassal, invited Dr. Voelcker to inform the meeting of the result of his contest with the Bedford Town Council.

Dr. Voelcker accordingly referred to the dispute he had had with the Bedford authorities. He said he had no wish to bring before the Society any matter of his own, and had simply taken up the question as one which concerned all public analysts. A full report of the case will be found on another page, but briefly the circumstances were these: In his capacity of public analyst for the borough of Bedford, Dr. Voelcker on one occasion had fourteen samples sent to him to analyse. Of these, thirteen were perfectly good, and one, a sample of coffee, was found to be adulterated with 80 per cent. of chicory. In returning the certificate of this adulterated sample, and of the others, he did not put in the weights of the samples. As a matter of fact, the weights had all been taken, although they were not mentioned on the certificates. On this ground the Town Council of Bedford, after several meetings, decided to refuse payment of the fees

for any of these fourteen analyses. The adulterated sample, they first said, they would make the basis of a prosecution, and after applying to him (Dr. Voelcker) to attend on a certain day, they wrote subsequently that they were sorry no prosecution could be instituted, because the certificate was informal. He offered to send an amended one; but the clerk to the Board, who happened to be a solicitor, said he was of opinion that after the certificate had once passed into his hands it could not be altered, so the prosecution would have to be abandoned. In the end the Town Council passed a resolution that none of the fourteen analyses should be paid for.

He (Dr. Voelcker) reported this to the Council of the Society of Public Analysts, who considered the decision absurd, and hoped he would put himself in communication with Mr. F. Low, the Hon. Solicitor to the Society, and fight the matter out.

He accordingly gave the matter into Mr. Low's hands, and on April 11th attended at Bedford with Mr. Low for the trial of the case in the County Court. It came before his Honour Judge Bagshawe, who, after an hour's discussion, reserved his decision, after expressing himself strongly of opinion that the plaintiff (that is, Dr. Voelcker) had no case at all. The report states that the Judge was satisfied that the certificate must be made out according to the statute, and after it had once left the analyst's hands he could not alter it. The Council's solicitor contended that the plaintiff had left out a material part by not inserting the weight, and the analysis was not complete until a proper certificate had been given. A further contention was, that they were entitled to a certificate for every sample, whether genuine or not, and that a letter to say a sample was genuine would not be sufficient; that they had entered into an arrangement with him, and until he had handed them a certificate legally made out, the work was not complete, and should not be paid for.

Although he (Dr. Voelcker) offered to be present so that no certificate would have been requisite at all, the Town Council said, "No; we are entitled to have a certificate which would enable us to dispense with your attendance and proceed without you."

Mr. Low requested the Judge to consider the question as to whether the certificate could not be amended, and the matter was then adjourned.

At the end of April he (Dr. Voelcker) received from Mr. Low a copy of the following letter, which had been forwarded to him from Bedford:—"Voelcker v. Mayor, etc., of Bedford. The judge has given judgment for the plaintiff for £19 19s., including the £6 6s. paid into Court; the costs are to follow the event, and payment is to be made in a month." This was a deduction of one guinea from the total amount of the claim. The costs were to be on the £20 scale. He was not able to say what the deduction of one guinea was for, whether for one certificate that was stated in Court not to be signed (though this was not stated in the pleadings), or for the one upon which it was alleged no prosecution could be instituted.

The PRESIDENT congratulated Dr. Voelcker on the result of the action, and thanked him for the public spirit with which he had acted in the matter, which was of interest to all public analysts.

On the proposal of Mr. CASSAL, seconded by Mr. STOKES, it was unanimously resolved that the thanks of the Society be tendered to Dr. Voelcker for the public spirit he had exhibited in carrying the matter to a court of law.

The PRESIDENT said he thought also they had good reason to be well satisfied with the way in which their Hon. Solicitor, Mr. Low, had acted in the matter.

At the next meeting of the Society the following, amongst other papers, will be read:—

“Condensed Milk,” by H. Faber.

“On the quantity of Volatile Acids present in Butter Fat,” by Dr. P. Vieth.

## ON THE IODINE ABSORPTION OF BUTTER FAT.

BY ROWLAND WILLIAMS, F.I.C., F.C.S.

(*Read at the Meeting, April, 1889.*)

PREVIOUS to Mr. Allen reading his valuable paper on “Some Abnormal Samples of Butter” before the Society of Public Analysts in December last (*ANALYST*, vol. xiv., p. 5) I had on a few occasions determined the proportion of iodine absorbed by the filtered fat of various butters submitted to me for analysis.

Since then I have applied the iodine absorption test to a large number of butters and butter substitutes, in the hope of obtaining information of a nature reliable enough to be of service in certain cases where the methods usually employed in the examination of butter have failed to give the analyst complete satisfaction.

It has, I think, been pretty well established by Mr. Allen and others that butter of a perfectly genuine character, but possessing somewhat abnormal properties, might be condemned as sophisticated, if, for instance, the analyst based his opinion too implicitly on the proportion of volatile and soluble fatty acids present in the sample. A knowledge of this fact has latterly placed chemists in an awkward predicament, in order to extricate themselves from which it has been thought desirable to examine minutely certain methods of analysis, more or less novel, as applied to the detection of adulterants in butter.

The particular point to which I have lately devoted a considerable amount of attention is, as indicated by the title of my paper, the question of the iodine absorption of butter fat, and although the results which I have obtained have not proved absolutely constant and conclusive, still I believe they are of sufficient interest and importance to justify me in bringing them under the notice of the members of this Society.

Before giving a description of my own results I ought, perhaps, to make a brief reference to a paper on “The Analysis of Fats and Oils,” read by Muter and De Koningh at the February meeting of the Society of Public Analysts, the first part of which is published in the current number of the *ANALYST*. I was not present at the meeting in question, but I gather from the partial report which has already appeared that the iodine absorption of the fatty acids, separated from butter fat by a special process, was one of the points dealt with. As my determinations of the iodine absorption were, however, all made on the pure butter fat, and not on certain fatty acids produced therefrom, as in the case of Muter and De Koningh’s experiments, our respective results are perhaps hardly comparable.

A short time ago, when I examined the most likely books of reference, in the hope





The above list contains representative samples of butter from several countries, although it is by no means as complete as I should have wished. An examination of the figures given in the table will show that, with one exception, the iodine absorptions of all the samples of butter fat were fairly concordant, the mean of thirty determinations being 35.34 per cent., with extreme limits of 23.6 per cent. and 40.3 per cent.

I am unable to give any satisfactory explanation of the former result. It was yielded by a butter, the genuine character of which I have no reason to doubt, judging both by the source whence it came and also by the results which were obtained on examining the sample by the usual methods of butter analysis.

The sample with the highest iodine absorption (40.3 per cent.) which I have recorded in the table was also, to the best of my knowledge, genuine butter, but, as only a partial analysis was made, I am unable to speak with absolute certainty upon this point.

Another sample, said to be German butter several months old, which was submitted to me for examination, had an iodine absorption of 52.4 per cent. The other analytical results obtained during the examination of this sample led me to the conclusion that margarine was present, and I reported to that effect.

It will, of course, be readily understood that I had a special desire to apply the iodine absorption test to butter known to be genuine beyond all possible doubt, but possessing decidedly abnormal properties, in order to ascertain whether the iodine absorption was affected to any extent.

Several samples which I had at hand gave more or less abnormal results as regards the volatile and soluble fatty acids, etc., but, strictly speaking, I could not guarantee their absolute genuineness.

A couple of months ago I accordingly wrote to Mr. Allen, asking him to kindly supply me with a small quantity of the abnormal butter referred to in his paper of December last. Mr. Allen informed me that he had none of the butter left, but as he had sent some to Mr. Estcourt, he advised me to apply to that gentleman, which I did. Mr. Estcourt was, however, unable to let me have any of his sample, so I have unfortunately not been able to carry out my intention in connection with a genuine abnormal butter.

This fact notwithstanding, I believe the figures which I have tabulated in this paper will in many cases be of considerable value to my brother analysts, and it is entirely with that object in view that I now publish the results of my experience with this particular process.

It has been suggested to me by a well-known butter merchant, for whom many of the analyses recorded above were made, that in summer the iodine absorption of butter may vary to a greater or lesser extent from that of butter produced in the same districts during the winter months.

This is a point which remains to be investigated, and if the results obtained are of sufficient interest, I shall be glad to bring them before the Society on some future occasion.

## "PURE" CHEMICALS.

By BERTRAM BLOUNT.

*(Read at the Meeting, April, 1889.)*

It is said that a bad workman finds fault with his tools, and the statement can hardly be disputed. It is, however, commonly found that a tacit deduction is made to the effect that he who finds fault with his tools is a bad workman, the fact that the converse of a true proposition is not necessarily true, being ignored. The resulting fallacy is frequently apparent, but in no instance is it more conspicuous than in the case of the chemist, where he is the bad workman, who is slow to find fault with and strive to improve his tools, wherever it is possible to do so.

Alive to the stress rightly laid by chemists on the importance of using reagents of the utmost attainable purity, manufacturers have long been in the habit of selling chemicals claiming to meet this requirement, and to distinguish them from less pretentious preparations have appended to them the titles "pure," "purif," "puriss," "chemically pure," "pure for analysis," and other reassuring terms. Rash is the analyst who relies on them, if anyone do. There is certainly usually a perceptible difference between them and the "commercial" kinds, but it is seldom absolute, and often wholly external. Much attention is paid to the appearance, packing, and above all to the labelling of such products, but with these their claims for consideration too often end, and one finds that if one desires something approaching purity, one must make it oneself.

A feeling not remote from disgust is produced, and leads the chemist to name his own preparations more modestly. Something of the sort probably induced Muir and Adie, in their recent paper on "The Interaction of Zinc and Sulphuric Acid" (*J. Chem. Soc.*, 1888, 47-58), to call their own admirable metal "approximately pure zinc," in contradistinction to the high-sounding titles used by the manufacturers from whom they obtained their raw material.

Similarly one finds in most laboratories the labels of reagents that have been prepared by the chemist himself, confining their assertions to some specific impurity, *e.g.*, "Hydrochloric Acid free from Arsenic," or particular process, such as "Calcium Carbonate for Lawrence Smith's alkali process."

If one be unwilling to undertake the tedious labour of preparing everything one has a difficulty in buying pure, and write to the maker supplying the offending article, mentioning its impurity, one usually finds that he is in no way disconcerted, but serenely admits that such is its normal condition. On further pressing he will perhaps confess that the hypercritical may detect room for improvement, and possibly volunteer the statement that he occasionally makes a small quantity of a still higher degree of purity, with an, if conceivable, more elaborate name—at a correspondingly higher price. On receipt of this it is commonly found that the improvement effected is by no means startlingly great.

As an illustration of the sort of thing I mean, I may quote a few figures from those obtained in the course of my own practice, in examining some of the reagents most largely used in the laboratory:—

In two samples of "pure" hydrochloric acid were found 0.328 and 0.118 grams.

per litre of solid matter, respectively; in three of "pure" nitric acid, 0.212, 0.66, and 1.084 grms. per litre; in one of "pure" sulphuric acid, 0.100 grms. per litre; in "pure" ammonium chloride, 0.23 per cent. of non-volatile matter containing manganese and lead. In "pure" ferric chloride I have found arsenic in notable amount, quite sufficient to prevent its use in Clarke's process for the determination of that body in copper (*J. S. C. I.*, 1887, 352). While speaking of ferric chloride, I may mention that the method one sometimes finds given (notably in "Crooke's Select Methods," p. 432), for freeing it from arsenic by repeated evaporation with hydrochloric acid, is utterly fallacious; it is based on the assumption that the arsenic is in the arsenious condition, an assumption which is not only unwarrantable, but inherently improbable. Purification can be effected by evaporating repeatedly with hydrochloric acid in presence of a suitable reducing agent, such as ferrous chloride, which may be conveniently prepared *in situ* by the addition of some iron wire.

Returning to my own unpleasant experiences, I have come across chromic anhydride which, when heated in blank with sulphuric acid, evolved sufficient gas of some sort to cause the potash bulbs to gain weight appreciably, and thus prove itself unsuitable for the combustion of carbon in iron and steel. In connection with this, I may recall the fact that Allen has mentioned the same difficulty (*Abstr. Proc. C.S.*, 56, 76), and overcomes it by preparing his chromic anhydride by the action of sulphuric acid on fused chromate of lead. This I have not tried, having for some time past abandoned the use of chromic anhydride in favour of the plan of burning the carbon in a porcelain tube, in a stream of oxygen from a cylinder of the compressed gas.

Though not strictly covered by the heading of this paper, I may mention that I have had to do with an iridio-platinum dish, which rapidly lost weight when heated empty in a muffle, with a stoneware jar which appeared to be lined with plaster of Paris, so persistently did calcium sulphate occur in the distilled water that was attempted to be stored in it, and with Nessler solution so insensitive, that sewage itself might feel secure from detection by it.

With regard to the practical bearing of all this: it may be urged that to insist on the necessity of examining reagents before using them, is to advance a platitude, and truly it is; but I submit that though such examination cannot be dispensed with, it ought not so constantly to lead to the detection of impurities. If a manufacturer undertake the preparation of pure chemicals, it is not too much to demand that his productions shall in some degree fulfil his promise. Certainly if a reagent be complained of, he will generally replace it; but the substitute is by no means necessarily any better than its predecessor, and, apart from that, the delay and annoyance suffered by the analyst, are in no way made good to him. It certainly appears to me within the pale of discussion as to whether the maker could not be sued for breach of the contract implied by the use of the terms "pure," "puriss," etc., on the label, and be cast in damages for any inconvenience or loss occasioned by a reliance on his statement.

Passing to suggestions for an improvement of such a state of things, the only one that occurs to me is some arrangement by which an enterprising maker, who was a thorough chemist, or employed one, could be induced to manufacture chemicals of as high a degree of purity as the analyst would prepare in his own laboratory, and with

similar specific limitations. By this I mean that if freedom from all impurities could not with any effort, commercially possible, be attained, yet a freedom from the special impurities that interfere with the main use of the reagent under consideration should be sought, and it should be labelled to that effect. That this is not without precedent is shown by the fact that assayers are supplied with lead and litharge, free from the specific impurity silver, which make no claim to be considered pure in other respects.

Further, if it be desired to obtain a pure product from a manufacturer less ideal than the one mentioned above, it is necessary to make plain to him that the handsome appearance of any reagent is valuable only if it be an index of purity, and that it is, by itself, an altogether secondary matter.

Laboratory, Broadway, Westminster, S.W., April 9th, 1889.

### SOME EXPERIMENTS WITH THE SOAP SOLUTION.

By ELWYN WALLER, PH.D., NEW YORK.

(Read at the Meeting April 10th, 1889.)

SOME little time since I had occasion to examine some samples of water, with a view to determining their comparative value for boiler and manufacturing purposes. With one of the samples especially, which was very hard, the soap test gave such unsatisfactory results that the method described by O. Hehner (ANALYST VIII. 77) was tried upon it, and in order to make the results comparable among themselves, the same method was applied to the other samples.\*

The results on the two hardest samples were as follows (sample A being the one especially referred to):—

HARDNESS (=  $\text{CaCO}_3$ ) IN PARTS PER 100,000.

| Sample. | BY SOAP TEST.        |               |               | BY HEHNER'S METHOD. |            |        |
|---------|----------------------|---------------|---------------|---------------------|------------|--------|
|         | Permanent<br>20 c.c. | Total 20 c.c. | Total 10 c.c. | Temporary.          | Permanent. | Total. |
| A       | 41.915               | 45.955        | 51.050        | 21.14               | 39.65      | 60.79  |
| C       | 31.31                | 33.30         | 34.845        | 19.20               | 19.93      | 39.13  |

Of course in the above, the 20 c.c. and 10 c.c. lots were diluted up to 100 c.c. with distilled water before applying the soap test.

Some of the other analytical results on these waters were as follows:—

PARTS PER 100,000.

|          | Analyst.   | Cl.   | $\text{SO}_2$ | CaO.  | MgO.  | Total Solids. | Loss on Ign. |
|----------|------------|-------|---------------|-------|-------|---------------|--------------|
| Water A. | Waller ..  | 1.633 | 28.10         | 26.85 | 4.829 | 86.5          | 8.0          |
| "        | Chemist C. | 3.00  | 28.76         | 26.74 | ..    | 88.1          | 6.0          |
| "        | " H.       | ..    | ..            | ..    | ..    | 81.3          | 17.6         |
| Water C. | Waller ..  | 1.100 | 12.02         | 15.31 | 3.280 | 49.0          | 8.0          |
| "        | Chemist C. | ..    | ..            | ..    | ..    | 60.7          | 5.0          |

\* *Lakmoid* was found to be more satisfactory as indicator in this case, than the phenacetolin indicator, recommended in Mr. Hehner's article.

I did not learn until some time afterwards that other chemists had also made examinations of samples of these waters a month or six weeks before mine was made.

The results which they obtained for hardness by the soap test were as follows:—

PARTS PER 100,000.

|            |            | Temporary. | Permanent. | Total. |
|------------|------------|------------|------------|--------|
| Water A .. | Chemist C. | 18·8       | 29·7       | 48·5   |
| " ..       | Chemist H. | ..         | ..         | 32·    |
| Water C .. | Chemist C. | 14·7       | 19·        | 33·7   |

As I had reported the results obtained by the Hehner method the discrepancy was very marked, especially in the case of water A.

Having noted that with different amounts of the water different results were obtained by the soap test, the idea naturally suggested itself to try the action of soap with different amounts of lime and magnesia. Accordingly a solution of pure double refracting spar was made after the regular method (solution of 1 grm. in hydrochloric acid, evaporating until neutral, and dilution to 1 litre). (This will be called "Ca solution.") A solution containing 2·46 grms. crystallised magnesium sulphate in 1 litre was also made (called "Mg solution"). A third solution, made by mixing 150 c.c. of each of the other solutions, was also prepared (called "mixed solution"). Different proportions of these solutions, diluted in every case to 100 c.c. with distilled water, were then tested with the soap solution.

The results were as follows:—

| c.c. of Solution diluted to 100 c.c. | Cubic centimeters of Soap Solution to Produce Permanent Lather after Standing. |      |                       |       |       |                   |      |      |  |
|--------------------------------------|--|------|-----------------------|-------|-------|-------------------|------|------|--|
|                                      | Ca Solution.   |      | Mg Solution.          |       |       | Mixed Solution.   |      |      |  |
| 5                                    | 10·7   | 10·8 | 12·15                 | 12·35 | 12·20 | 10·2              | 10·2 | 10·2 |  |
| 10                                   | 19·7   | 19·9 | 23·5                  | 23·3  | ..    | 18·3              | ..   | 19·7 |  |
| 20                                   | 37·7   | 37·8 | (35 to 40 uncertain.) |       |       | (27·5 uncertain.) |      |      |  |
| 30                                   | 54·  | 55·  | ..                    | ..    | ..    | ..                | ..   | ..   |  |
| 40                                   | (74 uncertain.)  |      | ..                    | ..    | ..    | ..                | ..   | ..   |  |

100 c.c. of distilled water required 1·3 and 1·4 c.c. soap solution to form a lather.

The figures in the last column for "mixed solution," were obtained by first adding 70 or 80 per cent. of whole amount of soap solution, which was finally used, mixing in without violent shaking, allowing to stand for 30 minutes, and then finishing the titration as usual. Where magnesium was present, care was taken to carry the test beyond the point where a temporary lather forms, mentioned by Wanklyn, and probably noticed by every chemist who has made much use of the soap test.

My usual practice has been to take the standard of the soap solution from the results obtained on 10 c.c. of the Ca solution, making no allowance for the action on the soap of the water used for dilution. That mode of calculating has seemed to give the

most accurate results that the soap test appeared capable of. Calculating the standard in this way, the value of 1 c.c. of the soap solution would be  $0.01 \div 19.8 = 0.000505$   $\text{CaCO}_3$ , but it is evident that a variety of different standards could be obtained from the above results on the Ca solution. Two different sets of standards would be obtained according as we deduct 1.35 c.c. for the influence of the water of dilution or not.

In the following tables, the columns headed "Ded't" give the results obtained by calculation, where this deduction is made:—

## Ca SOLUTION.

| Test made on | Soap required by 10 c.c. |        | Standard 1 c.c. Soap = $\text{CaCO}_3$ . |          |
|--------------|--------------------------|--------|--|----------|
|              |                          | Ded't. |  | Ded't.   |
| 5 c.c.       | 21.5                     | 18.8   | 0.000465                                 | 0.000532 |
| 10 c.c.      | 19.8                     | 18.45  | 0.000505                                 | 0.000542 |
| 20 c.c.      | 18.825                   | 18.2   | 0.000530                                 | 0.000549 |
| 30 c.c.      | 18.17                    | 17.71  | 0.000550                                 | 0.000564 |

The hardness of the Mg solution and mixed solution, expressed in terms of  $\text{CaCO}_3$ , would be as follows:—

| Test made on.  | Mg Solution.    |        |                                     |                       | Mixed Solution. |        |                                     |                       |
|----------------|-----------------|--------|-------------------------------------|-----------------------|-----------------|--------|-------------------------------------|-----------------------|
|                | 10 c.c. = Soap. |        | Hardness = $\text{CaCO}_3$ per c.c. |                       | 10 c.c. = Soap. |        | Hardness = $\text{CaCO}_3$ per c.c. |                       |
|                | c.c.            | c.c.   | Standard<br>0.000505.               | Standard<br>0.000542. | c.c.            | c.c.   | Standard<br>0.000505.               | Standard<br>0.000542. |
|                |                 | Ded't. |                                     | Ded't.                |                 | Ded't. |                                     | Ded't.                |
| 5 c.c.         | 24.46           | 21.76  | 0.0012352                           | 0.0011794             | 20.4            | 19.7   | 0.00103                             | 0.0010677             |
| 10 c.c.        | 23.4            | 22.05  | 0.0011817                           | 0.0011951             | 18.3            | 16.95  | 0.000924                            | 0.0009187             |
| 10 c.c. st'dg. | ..              | ..     | ..                                  | ..                    | 19.7            | 18.35  | 0.000995                            | 0.0009946             |

These results confirm the observations of Mr. A. H. Allen (December Meeting of the Society of Chemical Industry, vol. VII., p. 795), that the ratio of lime hardness to magnesia hardness by the soap test is not 2 to 3, or 42 to 75, as asserted by Wanklyn (*Water Analysis*, 7th Ed., p. 100); also that a mixture of calcium and magnesium salts shows a lower degree of hardness than either of them separate.

What remained of the sample of water A was then taken up after it had been standing  $3\frac{1}{2}$  months. It was again tested for total solids, hardness by *Hehner's* method, etc. The results were:—

|   | Total Solids. | Loss on ign. | Temp. Hard's. | Perm. Hard's. | Total Hard's. |
|---|---------------|--------------|---------------|---------------|---------------|
| When first received .. ..               | 86.5          | 8.           | 21.14         | 39.65         | 60.79         |
| After standing $3\frac{1}{2}$ months .. | 77.           | 9.           | 8.2           | 36.2          | 44.4          |

Some of this water was placed in a bottle, and tests were applied, as with the Ca and Mg solutions, diluting whatever amount was taken, up to 100 c.c., with distilled water before applying the soap test.

EXPERIMENTS ON SAMPLE A (after standing  $3\frac{1}{2}$  months).

| cc. of a taken. | c.c. of Soap required. |        | 100 c.c. of a = c.c. Soap |        | Hardness per 100000. |                             |
|-----------------|------------------------|--------|---------------------------|--------|----------------------|-----------------------------|
|                 |                        | Ded't. |                           | Ded't. | Standard = 0.000505. | Ded't. Standard = 0.000542. |
| 1               | 1.6                    | 0.25   | 16.                       | 2.5    | 80.800               | 13.550                      |
| 2               | 2.6                    | 1.25   | 13.                       | 2.25   | 65.650               | 33.875                      |
| 5               | 5.1                    | 3.85   | 10.2                      | 7.7    | 51.510               | 41.734                      |
| 10              | 8.75                   | 7.45   | 8.75                      | 7.45   | 44.187               | 40.379                      |
| 20              | 14.4                   | 13.05  | 7.2                       | 6.525  | 36.360               | 35.365                      |
| 30              | 19.8                   | 18.45  | 6.6                       | 6.15   | 33.30                | 33.333                      |
| 40              | 26.2                   | 24.85  | 6.55                      | 6.2125 | 33.077               | 33.672                      |
| 50              | 31.4                   | 30.05  | 6.28                      | 6.01   | 31.714               | 32.574                      |
| 60              | 37.4                   | 36.05  | 6.23                      | 6.008  | 31.478               | 32.573                      |

Which figure should be taken as representing the total hardness of this water?

The soap solution was entirely used up in making these tests, or they would have been carried farther. A small amount of another soap solution happened to be available, which like the first had deposited a slight sediment, which as before was filtered off, affording a clear, bright solution. With this tests were also made on the Ca solution. The results were:—

| Ca Solution used. | Soap Solution Used. |       |      | 10 c.c. = c.c. Soap. |        |
|-------------------|---------------------|-------|------|----------------------|--------|
|                   |                     |       |      |                      | Ded't. |
| 5                 | 10.85               | 10.85 | 10.9 | 21.73                | 21.23  |
| 10                | 20.5                | 20.6  | 21.  | 20.3                 | 19.45  |
| 20                | 37.                 | 38.1  | 38.  | 18.85                | 18.21  |
| 30                | 56.                 | ..    | ..   | 18.67                | 18.25  |

100 c.c. of distilled water took 1.2 and 1.3 c.c. soap solution.

The value of the soap solution was a little different from the first one, but the results show essentially the same as before.

The results by the soap test are apparently altogether unreliable, for very hard waters especially, and even with waters comparatively soft the results for permanent hardness are still more untrustworthy. This last point is alluded to by Mr. Wanklyn (*Water Analysis*, 7th Ed., p. 98) where he expresses disapproval of any attempt to determine the different kinds of hardness (temporary or permanent) by means of the soap test.

It would seem advisable to abandon the use of the soap test entirely, for although



all *chemists* are well aware of the roughly approximate character of the results, their clients usually are not, and attribute as much importance to the figure for "hardness by soap test" as to any other figure on the report of a chemist whom they may employ.

### APPARATUS FOR BUTTER ANALYSIS.

BY H. DROOP RICHMOND.

In a paper, a translation of which appeared in the *ANALYST* for November and December, 1888, and January and February, 1889, Wollny recommends the use of a 50 per cent. soda solution for saponifying the butter fat in Reichert's process, and the following apparatus has been found useful for storing this solution.

It consists of a bottle holding the solution fitted with an indiarubber cork, through which two tubes pass, one of them, open at both ends, carrying the blowing-ball A, and the other being bent over and terminating in the pipette B. The tube passes down inside the pipette, and terminates at a mark, to which, if the pipette is filled, just over 1 c.c. of soda solution would be discharged. In the upper part of the pipette at tube D, on which is the tap C, is joined at right angles, to the end of which a soda-lime tube is attached (not shown in figure). At the bottom of the pipette a cap (either of glass as in figure, or preferably of indiarubber) is fitted.

The apparatus is used in the following manner: On compressing the ball A, the soda solution is forced up the other tube into the pipette, the air escaping by the tube D (the tap being open). When the pipette is full to the mark, or a little over, the pressure on the ball is released, and the excess of soda solution, together with some air, is sucked back. The tap is now turned off and the cap removed, and the flask or other receptacle placed under the bottom of the pipette; on the tap being turned, the caustic soda solution runs out, and the cap being replaced, the apparatus is ready for use again.

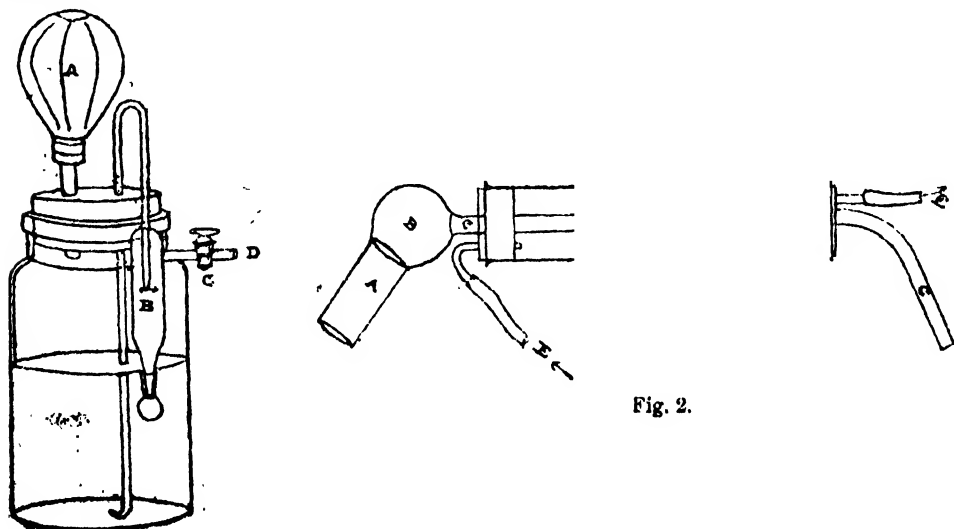


Fig. 1.

Fig. 2.

As long as the level of the caustic soda in the pipette is not allowed to rise as high as the tube D, no particular care need be taken to fill to any place, the excess being invariably sucked back. All the air that enters the apparatus must pass through the soda-lime tube attached to D, and is thus free from carbonic acid. The quantity 1 c.c. has been chosen, as it is sufficient for  $2\frac{1}{2}$  grs. of butter-fat, the quantity taken for the Reichert process; should 5 grs. be used, 2 c.c. may, of course, be taken.

Another piece of apparatus which will be found useful is this (Fig. 2), which is used when distilling. It consists of a tube, A 1 c.m. in diameter, and about 4 c.m. long, connected by a bulb, B 2 c.m. in diameter, with a tube C about 6 c.m. in diameter and 15 c.m. long, at angle of about  $120^\circ$ ; this at the end is also bent at  $120^\circ$ . On this tube C is fitted a small condenser D, the water running in at E and out at E'. The distilling flask is attached by a cork to A, and the end of C is inserted into a condenser, the water being allowed to run freely through D until the fatty acids are melted. When this is the case, the water is removed from D and the distillation proceeded with. The bulb B prevents any spurting that may take place, and the wide tube A allows the condensed liquid to run back into the flask without trouble. If care be taken to remove the water from D, the results are not sensibly different from those obtained with the Wollny apparatus.

*(Conclusion of the Society's Proceedings.)*

## ESTIMATION OF SOLUBLE AND INSOLUBLE FATTY ACIDS IN BUTTER

BY WILLIAM JOHNSTONE, PH.D., F.I.C., F.C.S.

Of the butter to be examined, 2.5 grammes of the clarified fat is saponified with a known quantity of alcoholic potash in a closed flask with the aid of heat and repeated shakings.

When saponification is complete, the soap solution is transferred to a suitable vessel and titrated with standard acid, and thereby the amount of KHO ascertained which is required to saponify the 2.5 grammes of the following three samples of butter.

| Thus—                    |                 |       | A.         | W.         | Y.         |
|--------------------------|-----------------|-------|------------|------------|------------|
| Alkali taken             | $\frac{N}{KHO}$ | .. .. | 25.00 c.c. | 25.00 c.c. | 25.00 c.c. |
| Acid required            |                 | .. .. | 14.78 c.c. | 14.96 c.c. | 14.76 c.c. |
| $\frac{N}{KHO}$ Consumed |                 | .. .. | 10.22 c.c. | 10.04 c.c. | 10.24 c.c. |

The alcohol is now boiled off, excess of acid added so as to decompose the soap, and then gently heated until the fatty acids are melted.

The insoluble fatty acids are now filtered off through an unweighed filter in the usual manner, and then thoroughly washed with boiling water until the washings are neutral, when the filter containing them is set aside in a moderately warm place and allowed to air dry. When the filter is sufficiently dry, it is taken and folded up and transferred to a Soxhlet extraction tube and thoroughly extracted with *dry ether*, the acids being received in an accurately weighed flask.

When the extraction is complete, the ether is evaporated off, and the flask and contents put in the water oven, and when dry allowed to cool and finally weighed.

Thus—

|                          | A.      | W.      | Y.      |
|--------------------------|---------|---------|---------|
| Fatty acid + Flask .. .. | 29.1917 | 29.1346 | 29.8400 |
| Flask .. ..              | 26.9430 | 26.8844 | 27.5942 |

|                                       |         |         |         |
|---------------------------------------|---------|---------|---------|
| Fatty acid (insoluble) in 2.5 grammes | 2.2487  | 2.2502  | 2.2458  |
| × 40 = Per Cent. .. ..                | 89.9480 | 90.0082 | 89.8320 |

When the percentage of insoluble fatty acids have been ascertained, add sufficient standard alkali to the flask, heat gently when saponification rapidly takes place, then wash the soap solution thoroughly into a basin and titrate again with standard acid and estimate the amount of alkali now consumed by the insoluble fatty acids.

Thus—

|                             | A.         | W.         | Y.         |
|-----------------------------|------------|------------|------------|
| $\frac{N}{KHO}$ Taken .. .. | 20.00 c.c. | 20.00 c.c. | 20.00 c.c. |
| Acid required .. ..         | 11.87      | 11.74      | 11.94      |

|                                |      |      |      |
|--------------------------------|------|------|------|
| $\frac{N}{KHO}$ Consumed .. .. | 8.13 | 8.26 | 8.06 |
|--------------------------------|------|------|------|

Then—

|   |            |            |            |
|---|------------|------------|------------|
| $\frac{N}{KHO}$ Consumed by 2.5 grammes butter    | 10.22 c.c. | 10.04 c.c. | 10.24 c.c. |
| $\frac{N}{KHO}$ Consumed by insoluble fatty acids | 8.13       | 8.26       | 8.06       |

|   |      |      |      |
|---|------|------|------|
| $\frac{N}{KHO}$ required by soluble fatty acid of 2.5 grammes .. .. | 2.09 | 1.78 | 2.18 |
|---|------|------|------|

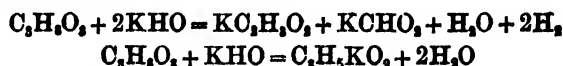
|   |      |      |      |
|---|------|------|------|
| The percentage of soluble fatty acid (as butyric) by Reichert-Wollny's process is:— |      |      |      |
|   | 4.37 | 4.44 | 4.68 |

The amount of soluble acids found in the above three samples of butter calculated as butyric acid:—

|                                   |            |            |            |
|-----------------------------------|------------|------------|------------|
|                                   | 7.35       | 6.26       | 7.67       |
| Deduct that found by distillation | 4.37       | 4.44       | 4.68       |
|                                   | <hr/> 2.98 | <hr/> 1.82 | <hr/> 2.99 |

Working in the manner above described, we get an accurate estimation of the amount of the total soluble fatty acids contained in a sample of fat, and it is, therefore, an infinitely superior process to Reichert's, for by the latter only a proportion of the soluble acids are obtained, and that merely of the *volatile acids*; besides, the Reichert-Wollny method only furnishes comparative results when rigidly performed in the same manner, a process which ought not to be tolerated when there is another method which gives with absolute accuracy the total amount of soluble fatty acids. Reichert's process certainly allows the operator to make a very rough estimation of the volatile acids, but it does not give him any insight as to the composition of the volatile acids, viz., as to the proportion of Butyric, Propionic, Acetic, and *Formic* acids, all of which are sometimes present in the distillate, and last, but not least, the proportion of non-volatile soluble fatty acids.

The following equations are extremely interesting, and may very easily be brought about with ordinary glycerine.



What must it be with nascent glycerine in presence of excess of KHO?

## RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

**TEST TO DISTINGUISH RESORCIN FROM CARBOLIC OR SALICYLIC ACID.** H. BOPDE *Nederl. Tydschr. v. Pharmacie*, etc., May, 1889.—If a few drops of a solution of sodic hypochlorite are added to a watery or alcoholic solution of resorcin, a violet colour, rapidly changing to yellow, is produced. On warming or adding excess of the reagent, the liquid gets dark brown. One part of resorcin dissolved in 10,000 parts of water will still show the reaction. Carbolie, salicylic, benzoic and other allied acids do not show the reaction, and at the most turn only slightly yellow on warming. Pyrocatechin, when treated with the reagent, turns a vanishing green; hydroquinon soon gets yellow and red. Another test is to first add a little liquor ammonia and then a few drops of the hypochlorite, when the liquid will give a reddish violet colour, which changes green on boiling. The colouring matter is not taken up by benzol. The reaction is not shared by salicylic acid, benzoic acid or antifebrin, but carbolie acid thus treated turns a greenish blue, which is partly decomposed by benzol. The colours are changed to red by dilute sulphuric acid.

L. DE K.

**COMPOSITION OF MACASSA OIL.** L. VAN ITALLIE.—*Nederl. Tydschr. v. Pharmacie*, etc., May, 1889.—The seeds of *Cussambrium spinosum* contain about 36 per cent. of a soft fat easily soluble in ether, petroleum spirit, and benzol, but slightly so in alcohol. On warming, the bulk of the fat melts at 22° C. The author obtained on analysis the following results: Iodine number 53. Insoluble fatty acids, 91·4 per cent. Specific gravity of these acids, ·922 at 15° C.; their melting point, 55° C. One gram. of the fat contained free fatty acid corresponding with ·0166 gram. caustic potash. The saponification equivalent was found to be 230. The glycerin was estimated by Hehner's bichromate method, and amounted to 6·3 per cent. The volatile acids were found to be acetic and butyric acids. The presence of oleic acid was proved by dissolving out the lead soap with ether and weighing the lead oleate. Some of the oil was saponified and the acids thrown up with hydrochloric acid. They were then treated with alcohol of 70 per cent. to remove bulk of the oleic acid, and then treated with alcohol of 90 per cent. The insoluble portion proved to be arachidic acid, whilst the neutralised solution gave with magnesium acetate a precipitate which, from its percentage of magnesia and other properties, was found to be a salt of lauric acid. The fat therefore consists of the glycerides of lauric, oleic, arachidic, acetic, and butyric acids. A sample of the oil which had been kept for twenty years had not in the least deteriorated.

L. DE K.

**ESTIMATION OF ALKALOIDS IN COCA LEAVES.** PROF. VAN DER MARCK. *Nederl. Tydschr. v. Pharmacie*, etc., April, 1889.—The author first tried Squibb's method. Fifty grammes of the leaves were macerated with 40 grammes of 95 per cent. alcohol and 1·6 gram. of hydrochloric acid. After percolating and distilling off the spirit, the residue was taken up with 30 c.c. of ether, which was then shaken with 30 c.c. of water and 1 c.c. of 10 per cent. acid. The watery fluid was drawn off, and the ether once more

shaken with 10 c.c. acidified water. The mixed acid fluid, after being once more shaken with a little ether to remove any colouring matter, was rendered alkaline with sodium carbonate, and the isolated alkaloid shaken out with ether. The author obtained .49 per cent. of alkaloid, but objects to the process on the following grounds: 1. The quantity of alcohol ordered is too small, and should be doubled. 2. As a rule, the ether, when shaken with acid water, forms a troublesome emulsion. 3. Twice shaking with ether is insufficient. 4. The residue left on evaporation is not pure cocain, as it did not dissolve completely in hydrochloric acid, and left about 50 per cent. of insoluble residue. It is also dangerous to distil a strongly acid alcoholic solution of cocain, as it so readily decomposes. The author next tried the process of Castaing. Fifty grammes of coca leaves were treated with 400 c.c. of boiling water, and after standing for half an hour percolated. The residue was then percolated with alcohol of 85 per cent., and the mixed filtrates thrown down with lead acetate. After the excess of lead had been removed with sodium sulphate, the liquid was concentrated, filtered, rendered alkaline with sodium carbonate, and shaken out with ether. The amount of cocain was .38 per cent., but it was only partly soluble in dilute hydrochloric acid, and much coloured. The next process tried was that of Albertoni and Guareschi. Fifty grammes of the leaves were exhausted with ether, the ether was distilled off, the residue treated with boiling water, and the solution evaporated to dryness with a little magnesia. On extraction with amylic alcohol, .14 per cent. of alkaloid was obtained. As a last resource, Bignon's process was tried. Fifty grammes of the powdered leaves were macerated for forty-eight hours with a 20 per cent. solution of sodium carbonate, then dried on the water-bath and exhausted with petroleum spirit to dissolve the cocain. The solution was shaken with dilute hydrochloric acid, which takes up the cocain. The acid fluid was then rendered alkaline and shaken with ether, which extracted the cocain. The percentage of cocain got by this process amounted to .06, a proof that most of the alkaloid had been decomposed by the strong alkali. The author then tried the following idea: 25 grammes of the powder were mixed with 10 grammes of magnesia and a little water, and dried on the water-bath. After percolating with ether (so as not to dissolve any hygrin), the ether was distilled off and the residue treated with acid water and filtered. After rendering alkaline, the alkaloid was extracted with chloroform. Obtained .2 per cent. alkaloid. A similar experiment was made with 50 grammes of the leaves, and .19 per cent. of alkaloid was obtained. Ether may, however, be advantageously substituted for chloroform. The author finally recommends the following process: 50 grammes of the powdered leaves are mixed with 20 grammes of magnesia, and dried at 60° C., then extracted with ether. After distilling off the ether the residue is taken up with 30 c.c. of 2 per cent. hydrochloric acid. The acid is filtered and repeatedly agitated with ether, to remove colouring matters. Ammonia is then added, and the mixture shaken out three times with 25 c.c. of ether. After standing for a little while over a few pieces of calcium chloride, the ether is evaporated and the alkaloid weighed.

L. DE K.

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ESTIMATION OF DEXTRIN IN NARCOTIC EXTRACTS. PROF. VAN DER MARCK. *Nederl. Tydschr v. Pharmacie*, etc., April, 1889.—The author tried Pannetier's process, which

apparently leaves nothing to be desired, and is performed as follows: Two grammes of the extract are dissolved in 50 c.c. of water and precipitated with 5 c.c. of liquor plumbi. The filtrate is freed from lead by sulphureted hydrogen, and concentrated to one-fifth of its bulk. An equal volume of spirits of wine is next added, which precipitates dextrin, and some alkaline salts. The precipitate is washed with alcohol, dried and weighed. To make sure, the dextrin may be inverted and estimated by Fehling's solution. Feeling no confidence in the method, the author tried the following experiments: Two grammes of extract of belladonna were dissolved in 50 c.c. of water, precipitated with liquor plumbi and filtered. After freeing the filtrate of lead and concentrating, alcohol was added and the fluid remained clear. Two mixtures were then made up containing respectively 5 and 10 per cent. of dextrin, but alcohol failed to produce a turbidity. With a mixture containing 15 per cent. of dextrin, a faint cloud was obtained, and, when 20 per cent. had been added, about one-third of the dextrin was recovered. On repeating the last experiment, but with addition of much more alcohol, 67 per cent. of the dextrin was recovered. The author, therefore, concluded that the method is perfectly useless, and endeavoured to find a better way. It is, of course, perfectly well known that dextrin, when heated with a 2 per cent. strong hydrochloric acid is gradually converted into glucose. Before applying the inversion process, it was necessary to prove: 1. Whether the extracts themselves contain copper reducing bodies; 2. Whether the inversion can be quantitatively depended on. Two grammes of belladonna extract were dissolved in 10 c.c. of water, and made up with alcohol to 75 c.c. The precipitate was filtered off and washed with alcohol of 75 per cent. The alcohol was evaporated, and the residue treated with Fehling, which was partly reduced. Fehling's solution was also reduced by the watery solution of the precipitate. Two grammes of the same extract were precipitated with liquor plumbi, the filtrate freed from lead by passing hydrogen sulphide, and after boiling neutralised. The liquid strongly reduced the Fehling. As these experiments proved that the extract contained reducing bodies, it became important to know the reducing power of different extracts from various origins. The author, therefore, took samples of extract of belladonna (Nos. 1, 3, 5, 7) and extract of hyoscyamus (Nos. 2, 4, 6, 8). Two grammes were dissolved in 50 c.c. of water and precipitated with 8 c.c. of liquor plumbi. After removing the lead, the liquid was evaporated down to 20 c.c. and titrated with Fehling's copper solution. It was now found that 10 c.c. of the filtrate (= 1 grm. extract) required of Fehling:—

|         |    |     |     |     |     |     |          |
|---------|----|-----|-----|-----|-----|-----|----------|
| Nos. 1. | 2. | 3.  | 4.  | 5.  | 6.  | 7.  | 8.       |
| ·7      | ·5 | 1·3 | 2·2 | 1·4 | 1·8 | 1·2 | 1·9 c.c. |

corresponding with an average percentage of ·8 per cent of glucose, which may be disregarded. The next step was to ascertain whether dextrin may be completely converted into glucose. Ten grammes of the best commercial dextrin were dissolved in 100 c.c. of water. Ten c.c. of this solution took an average of 9·6 c.c. of Fehling, corresponding with 5 per cent. of glucose. The sample lost in drying 11·6 per cent. of water; 2 grms. of the sample was dissolved in 100 c.c. of 2 per cent. hydrochloric acid, and heated for two hours in water of 90° C. After cooling, the liquid was made up to the mark and then titrated. 10 c.c. of Fehling required 23 c.c. of the liquid, which proved a loss of 8·8

per cent. dextrin. In a second experiment, when the heating was continued for three hours, the loss amounted to 18.9 per cent.\* These results are, however, more satisfactory than those obtained by Wertha and Payer, who respectively got a loss of 58 and 38 per cent. The author thinks, however, that this process may be still found useful in cases of serious frauds.

L. DE K.

COPPER IN GHERKINS. WESENER. *Zeitschr. f. Angew. Chemie*, No. 5.—One sample possessing an unnatural green colour gave on analysis .0036 per cent. of copper oxide, or .058 per cent. on the dried substance. A second sample of a yellowish-green colour only showed traces of copper, whilst a third sample seemed to be quite free from that metal. The copper in the first sample was no doubt the cause of the serious illness of a child. It will be interesting to analysts to read that not a trace of copper could be detected in the preserving vinegar.

L. DE K.

ESTIMATION OF ALKALOIDS IN EXTRACTS. L. VAN ITALLIE. *Nederl. Tydschr. v. Pharmacie*, etc., January, 1889.—Five grms. of the extract are dissolved in water with the aid of 10 drops of dilute sulphuric acid (1—20), and then made up to 50 c.c. After standing for an hour or two with occasional shaking, 25 c.c. of solution of lead acetate (1—10) are added. After settling, the fluid is filtered through a dry filter. 50 c.c. of the filtrate are now mixed with 10 c.c. of the dilute sulphuric acid, and again filtered. From this second filtrate 50 c.c. are put into a separating funnel, and after rendering alkaline with ammonia, shaken out three times with 50 c.c. of chloroform. The chloroform is distilled off, and the residue, after dissolving in 5 c.c. of spirits of wine, titrated with  $\frac{n}{100}$  hydrochloric acid, 1 c.c. of which represents .00289 gm. atropine or hyoscyamine, .0053 aconitine, or .00127 conine, lackmoid being used as indicator.

L. DE K.

ANALYSIS OF SULPHATE OF SODA. ISBERT AND VENATOR. *Zeitschr. f. angew. Chemie*, No. 3, 89.—The analysis of commercial sulphate of soda is very troublesome, and consequently highly charged for by analysts, which causes the manufacturers to send but very few samples. The authors have found a very accurate and simple process, which suits the manufacturers. It is as follows: About 2 grammes of the samples are dissolved in the smallest quantity of hot water and mixed with a little ammonia and ammonium carbonate as long as a precipitate forms. The precipitate must be freed from soda by re-dissolving in hydrochloric acid and reprecipitating with ammonium carbonate. The mixed filtrate and washings now contain sodium sulphate, ditto chloride, and also the excess of sulphuric acid the sample might have contained. The liquid, which will measure about 100 c.c., is evaporated in a platinum dish, to dryness. The residue is gently ignited to expel ammoniacal salts, and then weighed as pure sodium sulphate, any sodium chloride having been decomposed by the ammonium sulphate. If the sample should be rich in chlorine, a little extra ammonium sulphate should be first added to the filtrate. From the weight of the sodium sulphate is deducted the weight of sodium sulphate corresponding with the sodium chloride the sample contained, and which is estimated with deci-normal silver. The test analyses are very satisfactory.

L. DE K.

\* See also ANALYST, 1887, p. 138. L. de K.

## LAW NOTES.

## BOROUGH ANALYST V. THE BEDFORD CORPORATION.

This was an action in which Dr. Voelcker, of London, the Borough Analyst, claimed £21 from the Bedford Corporation for fees for making analyses. Mr. F. Low (Solicitor to the Society of Public Analysts), appeared for the plaintiff, and Mr. Bonsey (instructed by the Town Clerk) for the defendants.

Mr. Low, in opening the case, said no doubt his Honour was surprised that a public official of the Borough of Bedford should have to come to that Court to recover work done as public analyst, but public analysts generally, and particularly the Bedford analyst, were not popular officials, and Dr. Stevenson, the former borough analyst, terminated his engagement under circumstances which probably his Honour was aware of. [The Judge said this matter was perfectly immaterial to the action]. This was a material observation so far as his client was concerned, because he would not have taken the appointment had it not been for the persuasion of the late Ald. Howard, who was a friend of his. Dr. Voelcker was appointed as public analyst to the Bedford Corporation in May, 1887, on the condition that he was to receive one guinea for every sample submitted for analysis. In the following November various articles were sent to him from Bedford for analysis, and among them were two samples of coffee. Of the fourteen samples, thirteen were reported genuine, and no question could be raised on these, as no prosecution could follow. One sample of coffee was found to contain 80 per cent. of chicory, and in reporting this case Dr. Voelcker did not use the form of certificate as prescribed by the Act, and failed to insert the weight of the sample quite by accident, and in consequence of that the Corporation said it was useless to them as they could not take proceedings on it against the owner of the sample. But while refusing to pay for this one sample, the Corporation also refused to pay for the whole fourteen samples. With respect to the blank left for the weight, a foot-note on the certificate said that when the sample could not be conveniently weighed the weight need not be inserted, and he contended that it was perfectly immaterial, but it would not be so with some substances. The omission of the weight in this instance did not render the certificate useless, and he submitted that it was a good and sufficient statutory certificate under the Act. In the case of a prosecution, in case the Court did not accept the certificate, the presence of the Analyst would be all that was necessary, and he informed the Corporation he would be ready to attend if wanted. He also offered to amend the certificate, but the Corporation said that after the certificate had once left his hands he could not alter it. Six guineas had been offered by the defendants, but plaintiff would not accept it because he was entitled to twenty guineas, six other samples having later on been analysed.

The Judge said the point was as to whether the insertion of the weight was material in this instance.

Dr. Voelcker stated that he weighed the sample of coffee, and it weighed 5oz. In all cases of analysis of coffee, the weight was perfectly immaterial to the analysis, however small the sample might be. In some substances, such as drugs, weight was material.

Cross-examined: Had the sample been smaller, he should have retained it and asked for another sample, not for chemical reasons, but because it was always advisable to have a fair representative sample, but a very small sample from a large bulk might give a fallacious result. He examined every sample, and truly stated the result in the certificates.

The Judge expressed his opinion that it was the intention for the weight to be inserted in all cases, except where it could not be done.

Mr. Bonsey pointed out that one of the certificates was not signed, and was therefore useless. It was provided that in cases of articles liable to decomposition or change in constitution, mention must be made of it in the certificate, but in some of the certificates that came under this head this had not been done.

Mr. Low said it was unnecessary because all those samples were genuine.

Mr. Bonsey said that the object of the Act was that the form of certificate should be strictly complied with, and no proceedings could be taken before the production of the certificate properly filled up and signed.

The Judge was satisfied that the certificate must be made out according to the Statute, and after it had once left the analyst's hands he could not alter it.

Mr. Bonsey asked how they were to know that a proper sample had been sent if the weight was not stated. The plaintiff had left out the material part by not inserting the weight, and the analysis was not complete until a proper certificate had been given.

His Honour thought some of the certificates informal, but reserved judgment, and Mr. Low pressed his Honour to carefully consider the question of power to amend the certificate.

AN OLD QUESTION REVIVED.—A case of importance was heard at the Worship Street Police Court on the 9th ult., before Mr. Bushby, the presiding magistrate, against a tradesman who had been summoned at the instance of the Vestry of Bethnal Green for selling an article, to wit, coffee, adulterated with 60 per cent. of chicory, contrary to the statute, and was, therefore, not of the nature, substance, and quality demanded by the purchaser. Mr. Ogle appeared for the defence, and contended that his client was protected by the notice printed on the wrapper, that the article sold was a mixture. Mr. Lapworth, of the Sanitary Department, who appeared in support of the summons, addressing the magistrate, said this was the first case of the kind that had come under the notice of the Vestry, who



were desirous that it should be considered as a test case, and to have the decision of the Court upon it. The points to be considered were whether the sample was sold to the prejudice of the purchaser, as set forth in section 6 of the Act, and how far the vendor was protected by giving a label stating that the article was a mixture. It had been generally thought that if a customer asked for coffee the vendor might supply a sample containing any quantity of chicory, providing it is placed in a wrapper labelled, "A mixture of chicory and coffee." The wrapper produced by Mr. Ogle was itself an ingenious device; it was somewhat misleading, and was printed as follows: "The finest fresh-roasted coffee. This is sold as a mixture of chicory and coffee." It had been held by a metropolitan magistrate, in a recent case, that if coffee was asked for, the purchaser was defrauded if any other article was supplied, however it might be labelled. He would further call the attention of the magistrate to the case of *Liddle v. Reese*, and the judgment of Justices Lush and Manisty, the protection afforded to the vendor by the giving of a label, referred to in section 8 of the Act, applied to the sale of compounded articles of food mixed with any matter or ingredient not injurious to health, and not intended fraudulently to increase its bulk, weight, or measure. Coffee was not necessarily a compounded article, and where chicory was added, which could be purchased separately at about one-fourth the price, he respectfully submitted that the effect was fraudulently to increase its bulk and weight, and that, consequently, an offence had been committed against the statute. Mr. Bushby said, after hearing the evidence, that he was of opinion that the vendor had complied with the statute by giving a label, and that the case could not be sustained. If, however, a point of law were submitted to him, he would consider whether he should state a case for an appeal to a superior court.

**INTERESTING CASES OF THE ADULTERATION OF OLIVE OIL.**—At the Wandsworth Police Court, on the 17th ult., J. Palmer and Sons, Balham, were charged by Inspector Smith with selling olive oil so adulterated as to be indigestible, and consequently dangerous to health. The Inspector produced Dr. Muter's certificate, which showed that the oil was chiefly mineral oil, so prepared as to resemble olive oil in appearance. The defendant was fined £10 and costs.

At the same court, on the 1st of May, W. Taylor, jun., of Clapham, was charged by Inspector Smith with selling adulterated olive oil. Dr. Muter's certificate showed the article to contain not less than 50 per cent. of ground nut oil. The defendant pleaded entire ignorance, and the magistrate seeing that the article was not dangerous to health, let him off with 1s. fine and costs.

At the Southwark Police Court, on Wednesday, the 15th ult., before W. Slade, Esq., E. R. Goodrich, wholesale and retail oilman, 35, Old Kent Road, appeared in answer to a summons taken out by John Edwards, the Inspector for the District of St. George the Martyr, S.E. (on the certificate of Dr. Muter), for selling olive oil adulterated with 20 per cent. of cotton-seed oil. The defendant's counsel stated that he would plead guilty as he had had the oil analysed and found the certificate to be correct. The defendant had called in all the oil he sent out as olive oil as soon as he knew it to be impure, and he urged the magistrate to impose only a small fine. The Inspector stated to his worship that it was labelled "Finest Lucca Oil." The magistrate imposed a penalty of £5, and 12s. 6d. as costs.

## CORRESPONDENCE.

*[The Editor is not in any way responsible for opinions expressed by his correspondents.]*

*To the Editor of the ANALYST.*

### "NOTES ON LACTOSE."

SIR,—I very much regret that I was prevented from attending the March meeting of the Society when Mr. E. W. T. Jones read a paper upon "Lactose," as I certainly should have pointed out that a considerable portion of the results contained in his paper had already been published in the *ANALYST*, Vol. xi., page 27.

Mr. Jones' results, however, corroborate those obtained by myself. Thanking you beforehand for insertion of the above in your next issue.

13, Fish Street Hill, Eastcheap,  
London, 6th May, 1889.

Yours, etc.,

WILLIAM JOHNSTONE.

## ABNORMAL BUTTERS.

*To the Editor of the ANALYST.*

SIR,—I was under the impression that Mr. Estcourt was himself the authority for my statement that he had habitually employed, with his Westphal balance, a thermometer-plummet of which the bulb was broken, and which, therefore, gave him only arbitrary figures. I presume I may take Mr. Estcourt's last letter as an indication that I misunderstood him, but the use of a broken thermometer-plummet for observations at the boiling point of water is quite compatible with the simultaneous possession of an undamaged plummet for use at ordinary temperatures.

I did not give up quoting specific gravities of melted fats at 100° F. at the suggestion of Mr. Estcourt; but I did adopt the use of the Westphal balance, in place of the Sprengel tube I had previously employed, at his suggestion. Mr. Estcourt employed a bath of heated paraffin, instead of one of boiling water as adopted by me.

May 14th, 1889.

ALFRED H. ALLEN.

# THE ANALYST.

JULY, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

AN ordinary meeting was held at Burlington House on Wednesday, the 12th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

On the ballot papers being opened, it was announced that Mr. A. J. Hailes, F.C.S., had been elected as a member.

Mr. Cecil Howard, Public Analyst for the Strand District, was proposed for election as a member.

The PRESIDENT announced that the result of the ballot as to whether the summer meeting should be held in Paris or in Liverpool, was that the latter was preferred, and it would accordingly be held there, or in that district.

The following papers were read and discussed :—

"On Condensed Milk," by H. Faber.

"On the Quantity of Volatile Acids Present in Butter Fat," by Dr. Vieth.

"On the Amount of Volatile Acids in Butter Substitutes," by Otto Hehner.

## FAT EXTRACTION FROM MILK SOLIDS.

By H. DROOP RICHMOND.

(Read at Meeting, May, 1889.)

THE estimation of fat in milk, simple though it seems at first sight, has perhaps given more trouble to analysts than anything else, and on it, consequently, a very large amount of original work has been done. Happily, now the subject is much better understood than it was, and by the improved methods now in use something like concordance between separate analysts is to be reasonably expected. But there is still a want to be supplied, which is well expressed by Vieth (*ANALYST*, xii., 63; xiii., 49), where he says, "The difference between the percentages of fat extracted if the coil process is used . . . and the fat extracted if the plaster process is used . . . are smallest with skim milks, and increase with the increasing percentage of fat; or, in other words, the differences are small where great difficulties for the complete extraction of fat exist, and comparatively large where no such difficulties exist." Vieth gives two tables illustrating this: one in *ANALYST*, xii., 63, and the other comparing the results obtained by Hehner and myself in working out our formula (*ANALYST*, xiii., 49). A third table showing the same thing is found in *ANALYST*, xi., 62; and a glance at the diagram annexed to our paper (*ANALYST*, xiii., 24) shows it in a graphic form.

To explain this fact I undertook this investigation. I only propose to consider here the methods of extraction of fat from milk solids, and shall not, therefore, refer to such methods as Soxhlet's areometric process, etc.

The methods of fat extraction from milk solids are many, among them being :—

1. Wanklyn's direct extraction, and modifications by Carter Bell, Waller, etc.
2. Evaporation on Sea Sand.
3. " " Asbestos. Babcock (*Dept. Agric. Rept.*, 13, pt. I., 81).
4. " " Asbestos Cloth or Paper. Wiley (*Foods and Food Adulterations*, pt. I., p. 81), also used by Johnstone (*ANALYST*, xii., 234).
5. Evaporation on Plaster of Paris. Soxhlet.
6. " " Pumice, with grinding to powder. Storch (*ANALYST*, xii., 6).
7. " " Copper Sulphate. Morse, Piggott, and Burton (*ANALYST*, xiii., 18).
8. Evaporation on Sponge. Duclaux (*Le Lait*, p. 176).
9. " " Lint. Abrahams (*ANALYST*, ix., 20).
10. " " Paper. Adams (*ANALYST*, x., 46).
11. " " Powdered Glass. Baynes.
12. " " Kieselguhr.
13. " " Wood Fibre. Gantter (*Z. f. Anal. Chem.*)
14. Extraction from Milk Solids in pasty condition. J. Bell (*Foods*, vol. ii., and *ANALYST*, viii., 141).
15. Extraction from precipitated Casein.

It was at once seen that the investigation of all these methods would serve no useful purpose. It may be laid down as an axiom of milk analysis, that only methods which extract the whole of the fat are applicable, and no other should be tolerated as an exact estimation. The following published statements were found to assist in choosing suitable methods for investigation :—

1. Wanklyn's method and modifications are now universally admitted to be faulty.
2. By the use of sea-sand, Schrott and Hengold find results very nearly the same as Soxhlet's plaster and areometric methods ; other experimenters find rather less.
3. Kent and Grothe (*ANALYST*, x., 106) find that Babcock's method gives only slightly more than Wanklyn's, and  $\cdot 2 - \cdot 3$  less than Soxhlet's.
4. Wiley has discarded his asbestos paper method on account of it not giving results as high as Soxhlet's areometric method ; Johnstone has published figures (*ANALYST*, xii., 234) showing that results obtained by asbestos cloth fall appreciably below those given by Fleischmann's formula.
5. Soxhlet's method, which is the usual method of fat estimation on the Continent, gives very concordant results, which are higher than any of the preceding.
6. Storch's method gives on an average  $\cdot 27$  higher than Soxhlet's (*ANALYST*, xiii., 6 ; *Versuch. Stat.*, 1888, p. 316).
- 7, 8, 9, 11, 13, and 15. No comparative figures published for any of these methods.
10. Adams' paper methods gives higher results than any other, except Storch's (*ANALYST*, x., 46 ; Baertling, *Rep. f. Anal. Chem.* 41 (1886), No. 31, 411, etc.).
12. Neither method nor figures yet published.
14. Bell's method has been examined by Wigner (*ANALYST*, viii., 211), and gives  $\cdot 2 - \cdot 3$  more than Wanklyn's.

From these data I decided to submit to investigation the following methods:—

Soxhlet's plaster method.

Adam's paper „

and either Storch's pumice method or the Kieselguhr method, which are practically identical.

An objection has been urged against Adams' method on the ground that paper contains a substance which is soluble in ether, but difficult to extract; thus Vieth (*ANALYST*, x., 86) found that one coil gave, after soaking over night in ether, .0157 grs., and on a second extraction .0072 grs. more; and Faber (*ANALYST*, xii., 8); shows that in one case a first extraction gave .023 grs., and a second .010 grs. The instructions of the Milk Committee of the Society of Public Analysts (*ANALYST*, x., 217) are to previously extract the coils with ether, but nothing is said about there being any difficulty in extracting them completely, it being implied that twelve siphonings are sufficient. In a former paper, in which Hehner and I used this method for working out a formula, we stated that we did not previously extract our coils, but made a subtraction of .012 grs., that being the average amount extracted by blank experiments. Having now another batch of paper, the usual blank determinations were made, twenty-eight coils giving on an average .0102 grs. each, giving

a probable error for one coil of .0006 grs.

and a maximum error „ „ of .0025 grs.

Two coils were submitted to further extraction, with the following results, each being extracted for  $1\frac{1}{2}$  hours at a time:—

| 1st Ext. | 2nd Ext. | 3rd Ext. | 4th Ext. | 5th Ext. | 6th Ext. | 7th Ext. |
|----------|----------|----------|----------|----------|----------|----------|
| grs.     | grs.     | grs.     | grs.     | grs.     | grs.     | grs.     |
| .0102    | .0086    | .0076    | .0074    | .0012    | —        | —        |
| .0127    | .0025    | .0041    | .0032    | .0030    | .0020    | .0020    |

giving a total of .0350 grs. and .0295 grs. respectively. These results showed that although the subtraction of certain quantity found by blank experiment might do for every-day work, yet for a scientific investigation it is absolutely inadmissible. I tried the use of various other solvents; neither benzene, petroleum ether, or carbon disulphide showed any advantage over ether, but alcohol completely extracted the papers. As it has been stated that soap is used in the manufacture of the paper, I also tried the effect of acid, either by soaking the coils in dilute acetic acid, allowing to dry and extracting with ether, or by mixing a small quantity of glacial acetic acid with the ether or alcohol used for extraction, and found that in every case the paper was completely extracted. I found that the most convenient and expeditious method of extracting papers was to use acid alcohol, *i.e.*, alcohol containing 10 per cent of acetic acid, and extract in a large Soxhlet apparatus for three or four hours. Paper extracted in this way yielded to ether after about six hours' extraction a very small quantity of extract, consisting chiefly of fibres, amounting to perhaps one milligram., which if necessary may be estimated and subtracted, but which is practically negligible. After the completion of this stage of the research, my attention was drawn to a paper by Professor Soxhlet (*Molkerei Zeitung*, 43, 439), who had come to the same conclusions, and as the outcome of his work, Messrs. Schleicher and Schüll are placing on the market a fat-free paper, of which their agents in England, Messrs. Townson and Mercer, 89, Bishopsgate Street, E.C., hold a stock.

To prevent an objection similar to that urged against the paper process being brought forward against the plaster or Kieselguhr processes, I discarded the use of paper to wrap the cartridges in, and substituted wide test-tubes, having a hole at the bottom, and containing a wad of cotton wool which had been previously extracted with ether, until it gave no further extract. The Kieselguhr was ignited before use. The plaster or Kieselguhr, after being evaporated, was ground in the basin in which it had been dried, and *not, as is usually done, simply crushed to a coarse powder*; in many cases it was, after being extracted, ground a second time. The extractions in all cases lasted at least three hours, and in most cases more, as it was found that less time did not suffice, especially in the plaster extractions. For the sake of comparison, a series of results with unextracted coils were made, a correction of .010 grs. being used, and the extraction being prolonged for only  $1\frac{1}{2}$  hours (our usual custom hitherto).

The fine and repeated grinding and long extraction are essential points of Storch's method, and should always be adopted if very exact results are wanted.

The following are the results obtained:—

| No. | G.   | $\frac{G}{D}$ | T.    | Ad. Ext. | Ad. Un.   | P.    | K.    | Calc.  |        |
|-----|------|---------------|-------|----------|---|-------|-------|--------|--------|
|     |      |               |       |          |   |       |       | New F. | Old F. |
| 1   | 32.3 | 31.3          | 11.62 | 2.89     | 2.95  | 2.85  | *2.94 | 2.90   | 2.93   |
| 2   | 33.1 | 32.0          | 12.41 | 3.30     | 3.40  | 3.25  | *3.31 | 3.41   | 3.43   |
| 3   | 29.6 | 28.7          | 11.05 | 2.81     | 2.91  | 2.76  | *2.86 | 3.00   | 3.03   |
| 4   | 32.1 | 31.1          | 12.99 | 4.00     | 4.10  | 3.85  | —     | 4.11   | 4.14   |
| 5   | 32.0 | 31.0          | 12.90 | 4.02     | 4.15  | 3.96  | —     | 4.06   | 4.09   |
| 6   | 31.5 | 30.5          | 12.57 | 3.78     | 3.89  | 3.74  | *3.85 | 3.90   | 3.92   |
| 7   | 28.2 | 27.4          | 15.08 | 6.77     | 6.91  | 6.73  | —     | 6.73   | 6.78   |
| 8   | 31.2 | 30.3          | 11.07 | 2.66     | 2.81  | 2.66  | —     | 2.65   | 2.69   |
| 9   | 27.1 | 26.4          | 16.80 | 8.37     | 8.47  | 8.35  | —     | 8.43   | 8.49   |
| 10  | 30.2 | 29.3          | 11.82 | 3.45     | 3.49  | 3.41  | —     | 3.51   | 3.56   |
| 11  | 29.7 | 28.8          | 13.92 | 5.45     | 5.54  | 5.41  | —     | 5.43   | 5.47   |
| 12  | 31.1 | 30.2          | 11.10 | 2.75     | 2.88  | 2.70  | —     | 2.70   | 2.74   |
| 13  | 31.2 | 30.3          | 11.29 | 2.77     | 2.89  | 2.77  | —     | 2.84   | 2.89   |
| 14  | 30.8 | 29.9          | 12.57 | 3.94     | 4.49  | —     | —     | 4.03   | 4.07   |
| 15  | 31.8 | 30.8          | 12.06 | 3.35     | 3.54  | —     | —     | 3.38   | 3.42   |
| 16  | 30.3 | 29.4          | 10.52 | 2.41     | 2.62  | 2.40  | *2.49 | 2.38   | 2.42   |
| 17  | 30.7 | 29.8          | 12.49 | 4.03     | 4.22  | —     | —     | 3.98   | 4.03   |
| 18  | 31.6 | 30.6          | 12.24 | 3.61     | 3.78  | —     | —     | 3.58   | 3.62   |
| 19  | 29.8 | 28.9          | 11.98 | 3.80     | 4.00  | —     | —     | 3.74   | 3.78   |
| 20  | 31.5 | 30.5          | 10.35 | 1.99     | 2.10  | 1.96  | *2.02 | 2.00   | 2.02   |
| 21  | 32.8 | 31.8          | 12.69 | 3.86     | —   | 3.80  | *3.86 | 3.70   | 3.73   |
| 22  | 32.0 | 31.0          | 13.61 | 4.75     | —   | *4.75 | *4.79 | 4.67   | 4.69   |
| 23  | 33.8 | 32.7          | 9.21  | .54      | —   | *.54  | *.60  | .52    | .53    |
| 24  | 35.4 | 34.2          | 9.41  | —        | —   | *.46  | *.44  | .36    | .37    |
| 25  | 35.6 | 34.4          | 9.29  | —        | —   | *.26  | *.27  | .21    | .22    |
| 26  | 35.3 | 34.1          | 9.37  | .26      | —   | —     | *.26  | .34    | .35    |
| 27  | 32.5 | 31.5          | 11.47 | 2.68     | —   | —     | *2.71 | 2.71   | 2.76   |
| 28  | 35.6 | 34.4          | 9.71  | .42      | —   | —     | *.45  | .56    | .58    |
| 29  | 33.9 | 32.8          | 10.08 | 1.13     | —   | —     | *1.13 | 1.24   | 1.26   |
| 30  | —    | —             | —     | .35      | —   | —     | *.35  | —      | —      |
| 31  | —    | —             | —     | —        | —   | *.40  | *.44  | —      | —      |
| 32  | —    | —             | —     | —        | —   | *.20  | *.21  | —      | —      |
| 33  | —    | —             | 13.87 | 5.00     | 5.07  | 4.96  | †4.95 | —      | —      |
| 34  | 35.4 | 34.2          | 9.28  | .18      | $\left\{ \begin{array}{l} .15 \\ .28 \end{array} \right.$ | †.10  | †.12  | .25    | .25    |

\* Re-ground and extracted a second time.

† Extracted  $1\frac{1}{2}$  hrs. only.

1-20 were extracted for about three hours, the others 5—6 hours.

These results lead to the following conclusions:—

1. If a sufficiently long time is given for the extraction, and if the plaster and Kieselguhr are ground to a fine enough powder, there is, practically speaking, no difference between the paper, plaster, or Kieselguhr methods.

2. The use of unextracted coils induces an error which is by no means constant varying from +.06 to +.55. The observation that acids rendered a larger portion of the extractive matter of the coils soluble than would otherwise have dissolved led me to the conclusion that the free acid in milk (always present) increased the amount extracted from the coil itself, and this was further shown by the following experiment:—A skim milk, when fresh, gave as a mean of three results .15 per cent. fat. A day or two afterwards, when beginning to turn sour, the fat had increased to .28 per cent., the correction of .010 grs. being made for each coil.

I certainly recommend that the instructions of the Milk Committee should be modified, and should state that the coils should be extracted with acid alcohol, and that at least three hours or more extraction should be allowed.

As I have shown that the paper method, as Hohner and I worked it (and, we believe, as it was worked by many others), was open to objection, I deemed it advisable to see how my results agreed with the formula we had previously worked out, and which was based upon that method.

A discussion of the various formulæ which have been proposed will not be out of place here.

Behrend and Morgen (*J. f. Landw.*, xxvii., 250) were the first to point out the exact relation between sp. gr. fat and total solids, and published a table. In the same year, 1879, Clausnitzer and Mayer (*Forschungen auf dem Gebeite*, ii., 265) gave a formula, constructed from one sample of milk, which was analysed, allowed to stand during the night, and the skim milk again analysed. From this they found that 1 per cent. fat lowered the gravity .001, while 1 per cent of solids not fat raised it .00375. Hohner (*ANALYST*, viii., p. 129), from the result of 22 analyses of milk, compiled a formula to represent Wanklyn's method; he took the gravity of fat to be .9275, and assumed that 1 per cent decreased the gravity (water = 1,000) by .725, while each per cent. of solids not fat raised the gravity by 3.6. This assumption is not absolutely correct, though the error introduced is well within the limits of experimental error. Fleischmann and Morgen (*J. f. Landw.*, xxx., 293) constructed a formula to represent the plaster process. They assumed that each per cent. by volume (*i.e.*, gram. per 100 c.c.) of fat lowered the gravity by a constant factor; while each per cent. by volume of solids not fat raised it by a constant factor. They took the gravity of fat at 15.5 to be .94. From a series of experiments, Fleischmann found the gravity of butter fat to average .93, and consequently altered his formula in accordance with this fact. Hohner and myself last year published a formula for the Adams' process, in which we made the same assumption as in Hohner's original formula, but obtained our constants entirely from our observations. None of these formulæ are absolutely free from objection, as they either contain an assumption that is not strictly correct, or the gravity of the fat is assumed to be the same in milk as it is in the solid state.

On account of this, and the fact that the method employed by Hehner and myself is now shown to be faulty, I have considered it desirable to obtain a new formula.

If we assume that  $1+x$  is the gravity of a substance in solution, and that we have a solution containing  $y$  grs. in 100 c.c., the  $y$  grs. will occupy  $\frac{y}{1+x}$  c.c., and as the total bulk is 100 c.c., the water occupies  $100 - \frac{y}{1+x}$  c.c., and weighs  $100 - \frac{y}{1+x}$  grs.

$$\begin{aligned} \text{** The specific gravity of solution is } & \frac{100 - \frac{y}{1+x} + x}{100} \\ & = \frac{100(1+x) - y + y + xy}{100(1+x)} \\ & = 1 + \frac{xy}{100(1+x)} \end{aligned}$$

\*\* 1 gram. in 100 c.c. raises the gravity by  $\frac{x}{100(1+x)}$  which is a constant for each substance.

In a milk each gram. of fat in 100 c.c. lowers the gravity by a certain amount, ( $\phi$ ), while the solids not fat raise it by a certain amount ( $\sigma$ ); and if  $F$  = per cent. of fat,  $F \times D$  (density) = per cent. of fat by volume, and  $S \times D$  = per cent. of SNF by volume,

then  $G = S \times D \times \sigma - F \times D \times \phi$ , or  $\frac{G}{D} = S\sigma - F\phi$ ; or as  $S = T - F$ :  $\frac{G}{D} = (T - F)\sigma - F\phi$ ;

$$\text{or } \frac{G}{D} = T\sigma - F(\sigma + \phi); \text{ or } \left(\frac{\sigma + \phi}{\sigma}\right) - \frac{G}{D} = \frac{1}{T\sigma}; \text{ or } 1 = \frac{F}{T} \left(\frac{\sigma + \phi}{\sigma}\right) \dots \frac{G}{D} \frac{1}{T\sigma},$$

and, by the same process as used in the paper by Hehner and myself, I calculate from my results the following formula:  $T = 1.17 F - .263 \frac{G}{D}$ , which gives the following values:—

$$\begin{aligned} \phi &= .65, \text{ sp. gr. of fat } .939 \\ \sigma &= 3.8, \text{ sp. gr. of SNF } 1.613. \end{aligned}$$

In calculating this formula only the Kieselguhr results and the paper and plaster results of Nos. 22—29 have been used; the formula when applied to the paper results of Nos. 1—21 averages about .02—.03 per cent. higher.

It is a curious fact that the sp. gr. of fat in milk should be .939, which is distinctly higher than the observations of Blyth, Fleischmann, and others. This number is practically identical with the number calculated from the results obtained by Hehner and myself, and with that used by Fleischmann and Morgen. With regard to this it is worthy of note that Besana, from an extended series of analyses by Soxhlet's method, found that Fleischmann and Morgen's old formula expressed the results better than Fleischmann's new one; an examination of the results published in Fleischmann's paper (*J. f. Landw.*, xxxiii., 251.) shows the same thing; and Vieth practically confirms this in a paper where he states that with skim milks from 141 analyses he finds there is an average difference of + .04, which is about the difference between the two formulæ. It is, therefore, a remarkable fact that butter-fat has a higher gravity in milk (when presumably liquid) than it has when solid. Taking the gravity of milk-sugar to be 1.65—a number

obtained by many observers—of casein, etc. at 1.31 (Hehner), and ash at 3.0 (Dupré), and the proportions of these constituents in milk at 6 : 5 : 1 (Vieth), the gravity of SNF should be

$$\begin{array}{rcl} 1.65 \times 6 & & 9.90 \\ 1.31 \times 5 & & 6.55 \\ 3.0 \times 1 & & 3.0 \end{array}$$

$$19.45 \div 12 = 1.62$$

which is nearly identical with that given above.

When working out our formula, Hehner and myself attributed to lower results obtained with skim milk to the fact that a change in composition (due to formation of hydrates) took place as less and less fat was present, or as the amount of water increased. To ascertain if this was so, a sample of skim milk was taken and diluted with weighed quantities of water, the mixtures allowed to stand several hours, and the density taken. The density of the mixtures was calculated from the density of the original milk, and the amount of water added, with the result that the two were identical within experimental error.

| Percentage, by Milk. | Volume of Water. | Observed Sp. Gr. | Calculated Sp. Gr. |
|----------------------|------------------|------------------|--------------------|
| 100                  | —                | 1.03544          | —                  |
| 94.4                 | 5.6              | 1.03343          | 1.03345            |
| 89.3                 | 10.7             | 1.03170          | 1.03165            |
| 83.3                 | 16.7             | 1.02950          | 1.02952            |
| 79.8                 | 20.2             | 1.02829          | 1.02828            |
| 68.8                 | 31.2             | 1.02439          | 1.02438            |

In the table I have given in the two last columns, the numbers calculated by the new formula, and Hehner's and my old formula respectively, it will be seen that the difference between them is very small, and that for all practical purposes they are identical. By permission of the directors of the Dairy Supply Co., Mr. Faber has applied the new formula to over 200 analyses made by him in 1885 in the laboratory of that company by Storch's method, with the result of almost absolute agreement, there being an average difference of .02 per cent., with maximum differences of + .34 and — .26 respectively, showing that this method, which has been in use by Storch and other Scandinavian chemists for several years, gives complete extraction.

As the total solids are used for the calculation of the fat, it is, of course, important that they should be accurately estimated. The usual mode of doing this is to evaporate 5 grs. of milk to dryness in a small platinum, glass, or porcelain basin, these being used indiscriminately. With a view of shortening the process Gerber and Radenhausen in 1876 proposed the use of acetic acid (*Vorschläge zur einer einheitlichen Untersuchungsmethod der Milch* 7), but rejected it ultimately on account of the approximate character of the results, it being impossible to remove all the acetic acid, and at the same time to prevent change in the milk residue. Sea-sand and other powders have been used, Duclaux (*Le Lait*, 176) uses sponge, Babcock asbestos, and Adams paper, all with the idea of spreading the residue out in a fine condition, so that perfect desiccation may take place. When performing duplicate experiments, I was struck by the fact that when the milk was in a small basin the results were lower, and the residues darkened more than when a larger basin was used, and this was especially the case when the small basin was of



porcelain. A series of experiments was made to ascertain the influence of mass on the estimation, by comparing the results obtained with from 1–1·5 grs. of milk in a large basin and 5 grs. in a small basin. The results are as follows:—

| T. S.<br>5 grs. | T. S.<br>1 – 1·5 grs. | Diff. |
|-----------------|-----------------------|-------|
| 10·57           | 10·62                 | + ·05 |
| 12·33           | 12·41                 | + ·08 |
| 10·89           | 11·05                 | + ·16 |
| 12·79           | 12·99                 | + ·20 |
| 12·79           | 12·90                 | + ·11 |
| 12·53           | 12·57                 | + ·04 |
| 14·97           | 15·08                 | + ·11 |
| 11·06           | 11·07                 | + ·01 |
| 16·69           | 16·80                 | + ·11 |
| 11·70           | 11·82                 | + ·12 |
| 13·77           | 13·92                 | + ·15 |
| 11·05           | 11·10                 | + ·05 |
| 11·22           | 11·29                 | + ·07 |
| 10·25           | 10·35                 | + ·10 |
| 12·60           | 12·69                 | + ·09 |
| 13·42           | 13·61                 | + ·19 |

In every case the results obtained with small quantities in large basins were higher than the large quantities in small basins, and the residues in the former case were quite white, while the latter were more or less brown. Using small quantities only, from one to one and a-half hour's drying is requisite, although longer drying produces no change in weight, one, No. 2 in the list, having been allowed to remain in for six hours, showing not the slightest change; using the larger quantity constancy of weight is not obtainable. I am unable to account satisfactorily for this, but it seems to be connected with the rate of drying, the bulk of the water being evaporated in two or three minutes in the case of the small quantities, while it takes sometimes half an hour with the larger quantities. There is not the slightest difficulty in weighing out a small quantity of milk on a quick weighing balance, the loss by evaporation rarely being sufficient to influence the second place of decimals, and agreement between duplicates being extremely small (not exceeding ·05 per cent.). Wiley has made the same observation, and recommends in his book (*Foods and Food Adulteration, part i.*) either to dry about 2 grs. in a wide platinum basin or to dry 5 grs. on asbestos (*Babcock's method*). He finds that these two methods give identical results, which are higher than the usual method. Mr. Faber (private communication) informs me that he has dried 10 grs. of milk on 10 grs. of pumice, and finds that there is no loss of weight on leaving this overnight in the water oven. It is seen that there is a tendency to under-estimate the total solids, and, therefore, to over-estimate the water in a milk; this I mention because it has been used as an argument in favour of Soxhlet's method of fat extraction, that by its use complete analyses added up to about 100 per cent., Vieth (*Anal. xii.* 59) stating that his analyses add up to 100·15 on the average. I do not, however, propose to discuss this question here, beyond mentioning that Wiley (*Foods, etc., pt. i.*, 115) gives 121 complete analyses of milk, of which the average is

| Water. | Fat. | Proteids. | Sugar. | Ash. | Total. |
|--------|------|-----------|--------|------|--------|
| 87·22  | 4·07 | 2·73      | 4·90   | ·67  | 99·59  |

which is ·41 below 100 per cent. His estimations were made as follows:

Water : by drying 2 grs. in wide basin, or 5 grs. on asbestos.

Fat : Soxhlet's areometric process.

Proteids : nitrogen by either soda-lime or Kjeldahl,  $\times 6.38$ . (N.B.—Wiley uses 6.25, but I have recalculated his figures).

Sugar : polarised (Wiley's figures corrected for volume of fat).

Ash : as usual.

#### THEORY OF FAT EXTRACTION.

The difference between Adams' method and Soxhlet's method having now been shown, to be the result of, on the one hand, extraction of something, not milk-fat, and on the other, incomplete extraction, it only remains to explain, if possible, the theory of the subject. If an ordinary milk is filtered through filter or blotting paper, we find the portion that passes through is almost entirely free from fat, it usually containing .1-.2 per cent.; showing that by capillary attraction between the fibres of the paper the milk is almost entirely separated into two parts, one rich in fat, which remains on the surface of the paper, and the other poor in fat, which passes into the paper itself. Here are the conditions favourable for the complete extraction of the fat. Then again, the milk is spread out over an enormous surface, so that a very thin film is presented for extraction, but I consider that this condition is far less effective in promoting complete extraction than the first separation. In Soxhlet's process the milk is absorbed almost as a whole by the plaster of Paris, and the mass is dried together, so that there is by no means the separation that occurs in the Adams process. This mass is roughly broken up only, and consequently it is not surprising that complete extraction does not take place. With regard to the increasing difference with the increase of fat, the difference is only apparently an increasing one; for instance, say with a milk containing .5 per cent. of fat, there is a difference of .2 per cent., and with a milk containing 5 per cent. there is a difference of .4 per cent. At first sight there appears to be an increasing difference, while in reality, in the first case 40 per cent. of the fat is left behind, while in the second, only 8 per cent. And this is by no means surprising when we consider that almost the whole of the fat is distributed equally through the plaster, and that there is a great tendency for the plaster, etc., to enclose some of the fat, and the enclosing action would be greater the less the quantity of fat, and consequently there would be a tendency for a larger proportion of the fat to be left behind, although on superficial observation the amount of fat left in appears smaller. It is but natural to expect that by fine grinding and regrinding, and long extraction the enclosed portions of the fat should be brought into contact with the ether and become dissolved. It might be brought forward as an argument that the fat by long extraction becomes oxidised and therefore increases in weight; but this is excessively unlikely, and seems to be contradicted by the results of Johnstone (*Anal.* xi. 22), and the figures obtained by the use of the Abbé refractometer (for the loan of which I am indebted to Mr. Faber).  
Fats extracted by—

| Adams' method. | Soxhlet's (modified). | Kieselguhr process. |
|----------------|-----------------------|---------------------|
| 1.464          | 1.464                 | 1.463               |
| 1.4655         | 1.462                 | 1.465               |
| 1.463          | 1.463                 | 1.462               |

These figures are all normal for butter-fat. When, however, fats are heated in

contact with the air, the refractive index rises very perceptibly, thus a sample of butter-fat gave at first 1.463, after six hours in water-bath at 98°-99° C although the weight had not perceptibly changed, the refractive index was 1.467. I do not therefore think that that objection can be maintained; there was nothing extracted by ether from any of the materials used, the paper being extracted beforehand, the plaster giving nothing, and the Kieselguhr, having been ignited before use, also giving nothing.

In conclusion, I would recommend that extracted papers be always used for the Adams process, and that the extraction should be continued for 3-4 hours as a minimum; or that the Kieselguhr process should be used as an alternative; Kieselguhr presenting many advantages over plaster, it being of a porous nature, and easy to reduce to a fine powder, through which ether percolates with comparative ease; and that total solids be taken by drying 1.2 grs. of milk in a wide platinum basin on the water-bath for about an hour and a half, cooling and weighing; this on returning to the bath for another half hour, rarely shows more than one or two tenths of a milligram. difference.

On account of the practical identity of the new formula and the old one worked out by Hefner and myself, I do not give a table for facilitating calculation, the one published in our paper (*Anal.* xiii. 32), and also as a separate sheet, and the "milk scale" (*Anal.* xiii. 65) adequately serving that purpose.

I wish to express my thanks to Mr. Hefner, in whose laboratory this research was carried out, for the kind way in which he has advised and superintended the work, and to Dr. Vieth and Mr. Faber for the loan of instruments, books, etc., and for the way in which they have placed at my disposal a large amount of valuable information.

#### DISCUSSION.

MR. ALLEN said that Mr. Richmond had brought before them a large number of valuable results, which they would study at their leisure. It was a matter for great satisfaction that they had a young chemist amongst them who was not content simply with accumulating figures, but who also strove to ascertain how far they were due to avoidable experimental error, and how far to some error inherent in the process. Mr. Richmond's suggestion as to the presence of soapy matter in the paper was very plausible, but at the same time he (Mr. Allen) would like to know whether Mr. Richmond had succeeded in extracting any resinous or fatty matter from the paper. As to No. 14 experiment he should think that either the paper was full of soap or else the milk was.

With regard to the notes on the different factors for calculating fat, he thought that was a refinement which they scarcely required. He always used Hefner and Richmond's slide-rule, which usually gave satisfactory results, but after all the method was only one of a preliminary kind.

The questions of the size of the basins and so on were all eminently practical, and they were all indebted to Mr. Richmond for bringing the matter before them.

DR. VIETH said that as Mr. Richmond had alluded to him as being partially responsible that the paper was brought before the Society, he wished to say that he took with pleasure his full share of responsibility upon himself. He thought they had heard an extremely useful and important paper. The figures given bore out a fact which had never been shown before. They all knew that something could be extracted from paper, but here, for the first time, they had a large number of comparative experiments showing that a larger quantity of ether-extract was obtained when milk was dried up on paper extracted in the usual way, than in case the paper was extracted under certain precautions. The experiments answered a number of other questions, for instance, they proved that

plaster of Paris was after all a very good medium for drying milk previous to extraction. He thought the results with regard to the determination of the total solids were of almost more importance than the fat results. He was very much struck to hear that when a very small quantity of milk was dried in a large basin the results should come out higher than when a larger quantity was dried in a small dish. The experiments were most interesting and important, and opened up a new field for inquiries which were really wanted in that direction. With regard to the figures quoted from Dr. Wiley's report to the Commissioner of Agriculture, U.S., he must say that he considered the percentage of proteids so extremely low that he had some doubt whether the results could be correct. Personally he wished to thank Mr. Richmond for his valuable paper, which cleared up some hitherto rather obscure points.

MR. STOKES said that in the figures given of the three processes, if the fat was below 4 per cent. or thereabouts, those methods always gave a lower result than the calculation, whether by the new or the old table, whereas when you come to fats higher than 4 per cent., you always extract more than the calculation shows. With regard to dishes, Mr. Stokes thought some people made a mistake when they said "large"; and he illustrated this on the blackboard, showing that so-called "large" dishes had only higher rims but exposed no larger surface of the fluid. He advocated the use of flat-bottomed dishes.

MR. RICHMOND in reply said that he had not yet collected sufficient of the extract from the coils, but hoped to be able shortly to give some information respecting its composition; with regard to the formula he had brought forward a new one, more from the scientific point of view than from its having any practical advantage over the old one. Dr. Vieth had pointed out that the proteids in Wiley's complete analyses were very low, and he agreed with him there, but did not consider that the factor for converting nitrogen into proteids (6.38) was one on which any doubt could be shown, it having been established by Hammarsten and others for both casein and albumen in milk; he considered rather that, if there were a deficiency, it was more to be explained by Atwater's recent work on the soda-lime method, where he found that even experienced observers are often led into grave under-estimations. He did not consider that in plaster extraction a rich milk after one extraction was under the same conditions as a poor milk, for it must be remembered that in a rich milk the proportion of molecules of fat to molecules of diluent (in this case plaster and other milk solids) was much greater than in a poor milk, and consequently in the poor milk each molecule of fat was confined by many more molecules of diluent than in the rich milk, and so would be less easy to extract, and the extraction of some of the fat molecules in the rich milk could not make the others less easy to any marked degree. He had observed that with plaster the fat was extracted less readily than with either paper or Kieselguhr.

With regard to Mr. Stokes's objections to the formula, he thought that they arose from insufficient perusal of the results, as the formula had been calculated from the results themselves by a method which could not give other than agreement all along the curve, and was convinced that Mr. Stokes would see it in the same light when he had the paper before him and could study it at his leisure; he need hardly say, however, that he must not expect formulae to agree to .012. As to size of basins, he called a large basin one which exposed a large surface of milk to be evaporated, and a small one in which the opposite was the case. In reply to Dr. Voelcker he admitted that when milk drawn from the cow was not acid, he believed that it had the property of seeming both acid and alkaline at the same time, but by the time that it usually reaches the hands of the analyst it has become slightly but distinctly acid, due, no doubt, to the commencement of lactic fermentation.

[NOTE.—Since reading the paper I have examined the extract from the coils, and find it to consist chiefly of the calcium salt of a resinous acid, containing also sodium and small quantities of aluminium.  
—H. D. R.]

THE DISCRIMINATION OF THE VARIOUS SPECIES OF  
SACCHAROMYCETES.

BY WALTER J. SYKES, M.D.

*(Read at the Meeting, May, 1889.)*

THIS has been considered hitherto simply a matter of microscopic observation ; Rees and others have given descriptions and figures of the various yeast plants, but it has been recently shown by Hansen that each species of yeast is capable of assuming, under varying conditions of cultivation, etc., nearly all the forms which had been assumed as properly belonging to the others. Thus a circular, or nearly circular form is associated with the *Saccharomycetes cerevisiæ* group, an oval one with the *Ellipsoideus* group, and an elongated or sausage-shape form with the *Pastorian* group ; but as under certain circumstances *Sacc. Cerevisiæ* forms oval and spindle-shaped cells, and the others in their turn appear as circular cells, any absolute determination of their species by the microscope alone must naturally be futile. As will be seen further on, the ability to differentiate the various species of yeast is likely to become a matter of considerable importance, and one which the analyst ought to be prepared to undertake. Before going into the question of resolving yeast into its various species, it will be well to say a few words about yeast itself.

The true yeasts are simple unicellular plants belonging to the genus *Fungi*, and as they are capable of developing spores in cells called *asci*, they belong to the *Ascogenous* division of that genus. Yeast can reproduce itself under two distinctly different conditions ; the ordinary every-day one, where, immersed in a liquid capable of undergoing fermentation, it rapidly increases by a process of budding, never in this case forming spores. The other condition was first brought into notice by Rees in 1869, who found that by suddenly depriving yeast of all saccharine food, and placing it on the surface of a slice of potato or other moist porous vegetable root, in a very thin layer, budding still went on for a short time, but eventually ceased, and in a number of the cells spores were formed. Other observers obtained the same results by cultivating yeast on blocks of plaster of Paris, kept moist ; and this more convenient method is the one now universally employed for this purpose.

To Pasteur we owe our first definite knowledge of the relation of the organised ferments to the process of fermentation. He conclusively proved that fermentation only proceeds when the ferment grows and multiplies ; he also taught us that such organised ferments as the acetic, lactic, butyric, etc., together with *baccilli*, bacteria, etc., frequently contaminated our brewing yeast, and were the causes of what are commonly known now as the diseases of beer, viz., acidity, instability, ropiness, etc. He also very clearly pointed out the way to get rid of these troublesome invaders, and in this way did inestimable service to the brewing industry. He, however, states that when you have thoroughly purified a yeast, so as to be entirely rid of all adventitious organisms, you may yet obtain a yeast which gives a beer of bad flavour. This fact, which Pasteur left unexplained, has been entirely cleared up by the brilliant work of Dr. Hansen, the Principal of the Physiological Laboratory at Carlsberg, Copenhagen. He found that yeast, as ordinarily used in breweries, is an indefinite mixture of yeast plants of various species and varieties ; that the species and variety exercise a most marked influence on

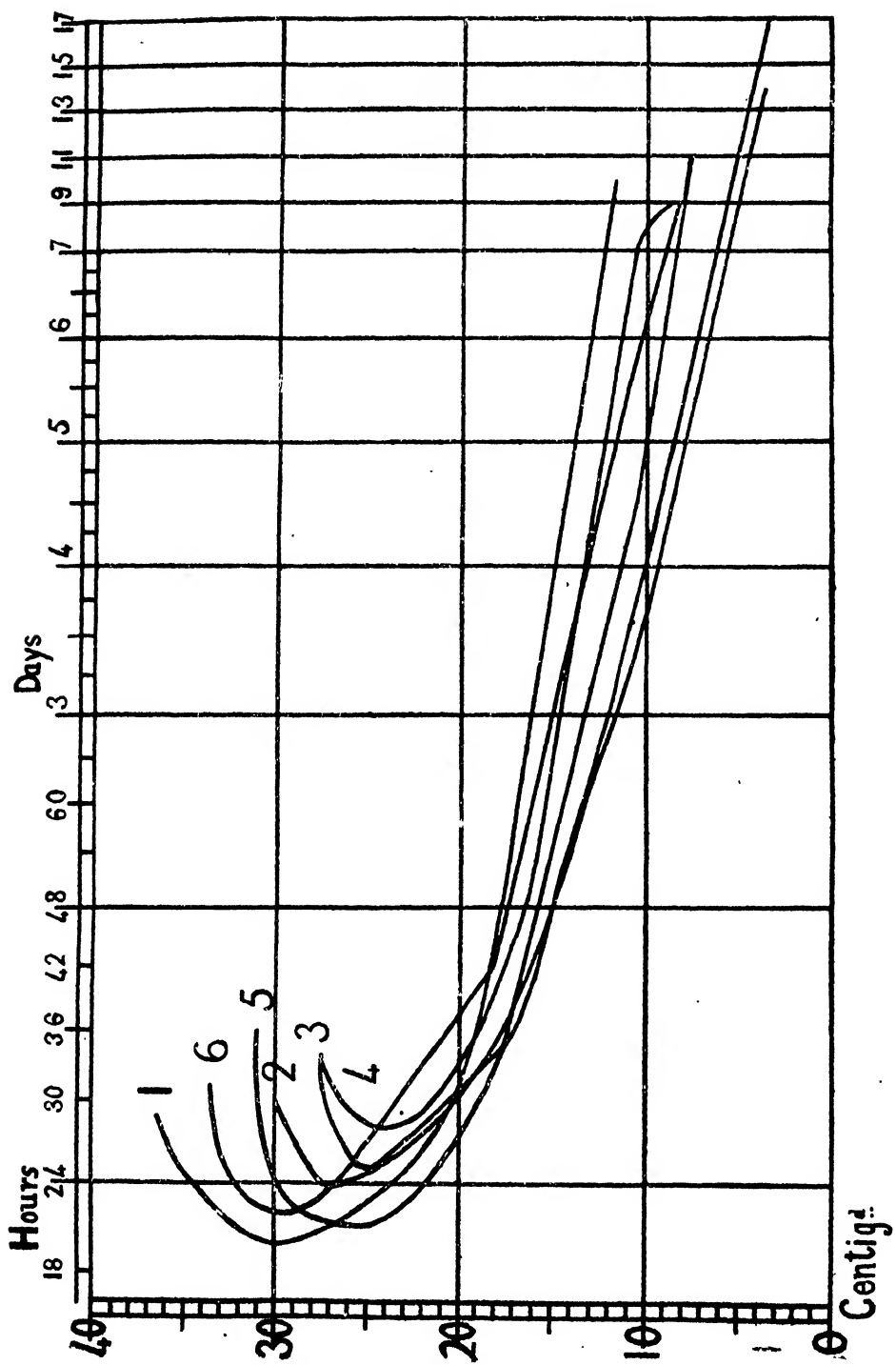
the flavour and properties of the finished beer, some causing a nauseous, bitter flavour others producing an article which will not clarify, others an unstable article, etc. He proposed to introduce into practice, and has actually done so, yeasts grown from a single cell, and therefore consisting of one distinct species only. The advantages of this system are obvious; the brewer, provided he takes care to use good materials, can invariably secure a beer of identical flavour and other properties. That this is not a mere matter of laboratory experiment is shown conclusively by the fact that these single cell yeasts have been used since the year 1884 in the Old and New Carlsberg Breweries, which produce annually over seven million gallons of lager and export beer, with the most marked success. In Denmark and Norway they are successfully used in all the largest breweries, to some extent in Sweden, Finland, Bohemia, and other parts of Austria, in Switzerland, North Italy, Belgium, North America, Russia, Germany, and Holland, in Asia and Australia. In all these breweries, with the exception of Baartz and Zoon, at Rotterdam, the system of low fermentation is adopted, *i.e.*, the type of yeast used is a bottom fermentation one, the fermentation being conducted at a temperature of 6 to 10° Cent.; the yeast sinking to the bottom of the fermenting vessel. The Rotterdam brewery employs the high fermentation system, which is the one almost, if not invariably, used in this country. In this system a yeast is employed which, as fermentation proceeds, rises to the surface, the temperature of the fermentation being from 10 to 15° Cent. So far the high or top fermentation yeasts have been very little studied, but as the advantages to be obtained by employing single-cell yeasts are sure to be recognised sooner or later in this country, a highly-interesting field of practical observation and research is opened out. The preparation of the small samples of the different varieties of single cell yeast will naturally fall within the province of the chemist; their multiplication to quantities sufficient for practical purposes, will take place in properly constructed apparatuses in the brewery.

The method devised at first by Hansen to obtain a sample from one cell was as follows: he diluted the yeast with water so that a measured quantity under the field of the microscope contained, say twenty cells. A quantity of this mixture, equal to that contained in the microscope field, was added to 20 c.c. of water and well shaken up. It was now assumed that one c.c. of this mixture would contain a single yeast cell. This quantity was next added to wort contained in a Pasteur or similar flask, and vigorously shaken, the remaining 19 c.c. being treated in a similar manner. The flasks were examined in a few days, and if bubbles were seen proceeding from one point only, the experiment was considered successful. If no sign of fermentation appeared, it was evidence that the c.c. of the mixture introduced had not contained a yeast cell; if bubbles arose from two or more points, that more than one yeast cell had been introduced, and naturally such flasks were rejected. This method had considerable elements of chance about it, and I only mention it as the one by which all Dr. Hansen's discoveries were made, particularly as it has been hinted by some of his detractors that his studies had their origin in Koch's gelatine plate cultivation process. This could not be the case, because all Dr. Hansen's facts were published before the latter's gelatine process had been announced.

After the publication of Koch's method, Hansen adopted a modification of it,

which leaves nothing to be desired in the way of obtaining cultures from a single yeast cell. He proceeds as follows: A sample of yeast is diluted as before with water until each microscopic field shows about twenty or thirty cells; a small drop of this mixture is now mixed thoroughly with 20 c.c. of ordinary beer wort containing 10 per cent. of gelatine. In all these processes it is almost unnecessary to state to my present audience that apparatus and fluids used must all be thoroughly sterilised. The gelatinized wort must never be allowed to reach a higher temperature than 25° Cent. at the time of the addition of the yeast cells or afterwards, for obvious reasons. A drop of this is spread in an even layer on an ordinary microscopic cover glass, placed film side downwards, on a small moisture chamber, containing a small quantity of water. The whole is placed under the microscope, and if the experiment has been successful, some half-dozen isolated yeast cells will be observed in different parts of the field, each of which is destined to form a colony. Those sufficiently apart are chosen from the rest, and a ring marked round them by a small apparatus which screws into the place of the object glass. A number is affixed to each circle with a fine pen, and the figure of each cell and its number noted down in the memorandum book. The moist chamber and its contents are placed in a warm place for 24 hours and further examined. Each cell will now be found to have formed a small colony; all the marked colonies are carefully examined, to see they are not likely to coalesce with adjacent ones, and that they are perfectly circular, great stress being laid upon this latter point by Dr. Hansen. After seeing that all is going on right, the moist chamber is allowed to stay another 48 or 72 hours, when the colonies will be found so large as to be easily seen by the naked eye. They are each in turn picked off the gelatine film on small pieces of platinum wire, which are dropped, colony and wire, into separate cultivation flasks containing wort. Fermentation and multiplication of yeast cells now commences, and all that is necessary is the careful periodical changing of the wort, so as to avoid outside contamination. By this means it is possible to increase the growth of yeast to any amount. The next question was to establish a method of differentiating the species with certainty, and this problem our indefatigable observer, Dr. Hansen likewise solved satisfactorily. By observing the occurrence of spore formation at different temperatures, he discovered that each species only developed spores between certain temperatures, and that at temperatures between these limits each species had its own relation to time and temperature. By taking the times of development as abscissæ, and the temperatures as ordinates, a curve may be generated for each yeast.

The accompanying diagram represents such a series of curves for six yeasts. For the abscissæ I have used a logarithmic scale of numbers, by which the initial curves are seen more plainly than if the ordinary numerical scale had been used. Spore formation is best observed in the following manner: A small truncated cone of plaster of Paris is moulded, the upper surface of which must be perfectly flat and smooth. On this surface, the yeast to be observed must be spread in a thin layer, the cone is placed base downwards in a vessel, and water poured in until it reaches halfway up the side of the cone. The whole is loosely covered, so as to admit of free aeration, this being absolutely necessary for spore formation, and kept at an even temperature. Small samples are taken off the surface of the cone from time to time and examined under the micro-





scope ; the time to be noted is the earliest sign of spore formation. It has been found that only young and vigorous cells sporulate ; care must be taken, therefore, to secure these by growing the sample for 24 hours in good, well-aerated wort, carefully pouring this off, and adding a fresh supply of wort. After another 24 hours the wort may be carefully poured off the thick layer of yeast at the bottom of the vessel, and the latter spread on the plaster block as described above. In this manner Hansen has differentiated six species of yeast, *Saccharomycetes Cerevisiæ*, a top fermentation yeast, having its times of spore formation as follows :—

*Sacc. Cerevisiæ I.*

|       |     |     |     |                     |
|-------|-----|-----|-----|---------------------|
| 37.5  | ... | ... | ... | No spore formation. |
| 36.37 | ... | ... | ... | 29 hours.           |
| 35    | ... | ... | ... | 25 "                |
| 33.5  | ... | ... | ... | 23 "                |
| 30    | ... | ... | ... | 20 "                |
| 25    | ... | ... | ... | 23 "                |
| 23    | ... | ... | ... | 27 "                |
| 17.5  | ... | ... | ... | 50 "                |
| 16.5  | ... | ... | ... | 65 "                |
| 11-12 | ... | ... | ... | 10 days.            |
| 9     | ... | ... | ... | No development.     |

*S. Pastorianus I.*, a bottom fermentation yeast, which frequently occurs in the air of fermenting rooms, and gives a strong, bitter taste to beer.

*S. Pastorianus II.*, feeble top fermentation yeast, does not seem to give rise to any disease in beer.

*S. Pastorianus III.*, top fermentation yeast, causes yeast turbidity.

*S. Ellipsoideus I.*, bottom fermentation yeast, found on the surface of grapes.

*S. Ellipsoideus II.*, bottom fermentation yeast, causes great turbidity.

As the whole nomenclature of yeasts is at present in a state of transition, these names must be looked upon as merely provisional.

In addition to the before-mentioned discoveries in spore formation, Dr. Hansen observed some curious facts with reference to the formation of yeast films on the surface of a yeast cultivation when fermentation had quite ceased. Each yeast seems capable of forming a film, which appears at a longer or shorter period of time for each species. Temperature effects a similar acceleration or retardation, as in the case of spore formation, and consequently the conditions of film formation may be used to corroborate those of spore formation.

From the foregoing we conclude that diseases of beer are not only caused by false ferments, but also by *saccharomycetes* ; that it is possible to distinguish the useful from the noxious species of the latter ; and that it is easy to prepare a yeast which shall consist of one species only, thus affording the brewer an exactitude and certainty in his fermentation results he never possessed before, and at the same time opening out a wide and interesting field for the analyst.

#### DISCUSSION.

The PRESIDENT said he would like to know if Dr. Sykes could explain definitely the cause which determined the matter as to whether a yeast became a top or a bottom

yeast. Was it due to an entirely different kind of cell, or was it due to the circumstances under which the cell was placed? Had Hansen's researches confirmed the belief a yeast became top yeast, when by its treatment the growth was encouraged and became vigorous, or on the other hand bottom yeast when its growth was checked. Of course it was understood that top yeast fermentation took place at a higher temperature, and that in proportion the growth of the yeast plant was more rapid, and thus gas was formed more abundantly, which, by adhering to the yeast cells, rendered them buoyant and carried them to the top, so forming top yeast; but with the lower temperature and less vigorous growth and less gas formation, bottom yeast resulted.

With respect to the modification which Hansen has shown by his experiments to be capable of cultivation, is it not true that these varieties are very unstable, and readily revert to the ordinary type?

He, the speaker, would like also to ask Dr. Sykes whether he had any knowledge of the enduring qualities of the ascospore formation, as compared with the ordinary method of reproduction. From a biological as well as a sanitary point of view, the matter was of great interest to him.

Mr. RICHMOND, bearing in mind that Dr. Sykes had stated that *Sach. Pasteureanis* I. gave bitter taste to beer, would like to know if the substance giving this taste was precipitated by acetate of lead, otherwise it might interfere with the detection of foreign bitters.

Mr. CASSAL asked if they were to understand that one sort was absolutely incapable of being converted into any other sort? He would like to know if any experiments had been made with a cell as to its capability of altering its original constitution as evidenced, for example, by the appearance of abnormal products, such as the bitter substance which had been alluded to. It had been asserted in regard to micro-organisms obtained from "pure cultivations," that they were incapable of change in this respect, but he greatly doubted whether there was sufficient evidence to warrant such a statement.

In reply to the President's questions Dr. Sykes said the attempt to transform one species of yeast into another had been tried in every conceivable way by Hansen, and found impossible; he considers that the species are as distinct and definite as that of any of the higher fungi. You may cultivate high yeast at a low temperature, but though it sinks like a low yeast, fermentation proceeds much more slowly than in the case of a bottom fermentation yeast; if placed in its normal fermentation temperature, and especially if well aerated, it quickly resumes its former properties. In making a gelatine cultivation of a yeast known to be of one species, you might find two colonies of cells of entirely different shape, as, for instance, one oval, the other sausage-shaped. If these were introduced into two flasks, and a cultivation started, though the whole cells formed at first would be of the same shape as their progenitors, yet sooner or later this speciality of form would entirely disappear. With reference to the spores of yeast they are remarkably persistent. About a year ago he had found that they existed in large quantities on malt, which is generally exposed to a temperature of 200° to 220° F. for several hours during the final stage of drying on the kiln.

In reply to Mr. Richmond's question, he did not know whether the bitter generated by *S. Pastoriensis* I. was precipitable by acetate of lead or not.

In reply to Mr. Cassal, Dr. Sykes saw that whatever changes took place in the shape, etc., of the cells by different methods of cultivation, their chemical properties remain unaltered; a *Cerevisiæ* would always produce a good flavoured beer, a *Pastoriensis* I. would invariably give one of bad flavour.

*(Conclusion of the Society's Proceedings.)*

## ON THE ESTIMATION OF STARCH.

BY PROF. DR. ALEX. VON ASBÓTH.

HAVING to attend to many professional duties, I have been prevented from sooner completing my investigations on the estimation of starch in cereals. Last July (see ANALYST, 1888) I proved by several experiments that in working with pure starches, the results obtained by Lintner's process and my baryta process were concordant. I therefore concluded that equally concordant results would also be obtained in dealing with cereals, but I was much mistaken. I experienced the same thing as Monheim, who found in the same sample of wheat 69.06 per cent. of starch by my process, and only 62.08 by Lintner's. I then began to think whether cereals might not contain other baryta absorbing bodies, and at first suspected the proteids, but afterwards found these not to interfere. After many experiments I found the enemy to be fatty matter.

It seems that the fats contained in cereals contain free fatty acids, or these acids are in such loose combination with glycerin, that they are easily saponified by the baryta water. This being so, it was easy enough, so to modify the process, as to render it fit for the analysis of cereals. The flour must be first extracted with ether, which I do as follows:—Ten grammes of the substance are put into a filter paper cartridge and exhausted with ether in the Soxhlet in the usual manner. The solution is evaporated to dryness and the fat weighed. The contents of the cartridge are now put on filter paper and exposed for about an hour, so as to let every trace of ether go off. The flour is then thoroughly mixed in a porcelain mortar, and is then ready for analysis. A few grammes are used for the estimation of moisture, and 1 or 1.8 grm. is used for the treatment with baryta. This modification of the process involves a little calculation, of which I give an example. From a sample of finely ground wheat I took 10.0235 grms. for the estimation of the fat. Obtained .1785 grm. fat amounting to 1.78 per cent. The moisture of this sample dried at 110° C. came to 13.29 per cent. From the *extracted* flour I weighed 1.511 grm. and, after gelatinising it as directed, added 50 c.c. of baryta water and made up to the mark with 45 per cent. alcohol. 10 c.c. baryta water = 29.53 c.c.  $\frac{N}{10}$  hydrochloric acid\*; 50 c.c. of filtrate = 23.04 c.c. acid = 69.58 per cent starch. The moisture of the extracted flour being only 11 per cent., we have:—

$$a. (100 - 11) : 69.58 = 100 : x$$

$$x = 71.17.$$

$$b. 100 : 78.17 = (100 - 13.29 + 1.78) : x$$

$$x \text{ (or the starch in original sample)} = 66.37 \text{ per cent.}$$

I now also analysed the sample by Lintner's process, but could not get the results to agree, but as they agreed when dealing with pure starches, I began to suspect Lintner's process when applied to cereals. I therefore tested the residue which was left in the high pressure flask. On moistening with iodine, a blue colour was developed, and that even after heating for six hours at 140—145° C. As however cellulose also gives sometimes a blue with iodine, this test was not considered sufficient, and I therefore heated the residue with perfectly pure diastase for 12-24 hours at 65-70° C. The filtrate

\* I now prefer to first use  $\frac{N}{10}$ -acid, and when nearly enough of this has been added, I use  $\frac{N}{100}$  acid. With care .005 c.c. of a  $\frac{N}{10}$ -acid may thus be read off.

strongly reduced the alkaline copper solution. I also have made experiments to quantitatively estimate the starch in the residue and operated as follows:—The precipitate which had collected on the glass wool was rinsed into a flask, and mixed with a solution of .02 grm. of diastase. The whole was then heated for 24 hours at 65-70° C. in a water bath. I then filtered off and diluted up to 100 c.c., then added 10 c.c. hydrochloric acid and heated one hour in boiling water. The liquid was next neutralised with barium carbonate, and evaporated to dryness in the water bath. The residue was then exhausted with alcohol of 90 per cent., filtered off, again evaporated, and the sugar finally estimated with Fehling's solution. The result could not be right, because it is not to be taken for granted that all the starch had dissolved, and the inversion process was done in too short a time, but I did not wish to heat longer so as to prevent decomposition of the diastase by the acid, which would yield sugar. However, I still obtained from the residue .83 per cent. of starch, calculated on original substance.

*(To be continued.)*

### PEPPER ADULTERATION.

BY F. WALLIS STODDART.

THE form of pepper adulteration described in a note appearing in an earlier number of this journal (*ANALYST*, xiv., 37), is still largely employed, but the "make-weight" now principally introduced appears to be steatite in fine powder, which is added to the pepper to the extent of 10—15 per cent.

The proportion of chromate of lead remains about the same, and can, I find, be detected more readily in the ash than in the chloroform residue; for the latter not only contains a good deal of pepper-starch, which interferes with the boiling, but also apparently some substance which renders the tests for chromic acid uncertain. One or two grammes of pepper yields excellent results when treated in this way.

The feebleness of the present Act is well illustrated by the powerlessness of the authorities to deal with this fraud; for, though the manufacturers are perfectly well known, and numerous convictions amongst their customers have taken place, as they do not reside in Bristol the local authorities decide they can do nothing with them; and, as in each case they openly offer to pay all fines and expenses, and, where necessary, even to salve the wounded reputation by a small honorarium, they are not likely to lack business.

### LAW NOTES.

**BATTLE OF THE PHARMACOPŒIAS.**—At the Bow Street police-court, on May 27th, Charles Ferdinand Keele, chemist, of Tottenham Court Road, was summoned for selling sal volatile not prepared according to the requirements of the British Pharmacopœia.—Mr. Smith appeared to support the summons; Mr. Forrest Fulton for the defendant.—On the 6th April, six ounces of sal volatile were bought at the defendant's shop for 3s. It was analysed by Dr. Redwood and found to contain less alcohol and less spirits of ammonia than were required by the Pharmacopœia Britannica. Some question arose as to the Act under which the summons was taken out, the Food and Drugs Act, and not the Pharmacy Act.—Mr. Fulton said it was matter of common knowledge that the new Act now before Parliament would incorporate the two Acts. His client was not a "compounder" of this drug, but simply a retail vendor. What he sold was also what was described as sal volatile, although under another name in the Pharmacopœia Londonensis.—Mr. Vaughan asked to have some professional evidence on which to go, and Dr. Redwood was then called. He was asked by Mr. Vaughan what sal volatile should be, and replied, "A solution, partly aqueous and partly spirituous, of carbonate of

ammonia, with certain essential oils of nutmeg, cinnamon, and lemon, thereby constituting a stimulating alkaline solution."—Mr. Vaughan: But in those ingredients I don't notice where the alcohol comes in.—The witness: Estimating it as a rectified spirit, there should be one-third.—Mr. Smith: But as a medicine, what is the most important?—Witness: The ammonia.—Mr. Vaughan: But what is the alcohol for?—Witness: To keep the oils in solution. In the present sample there was less than half what there should have been of alcohol.—Mr. Vaughan: What is the test?—Witness: The great test is the power of neutralising oxalic acid.—Cross-examined by Mr. Fulton: Sal volatile was first used in medicine in 1720. It dropped out of use until 1885. It was mentioned under another name in the last edition of the Pharmacopœia Londonensis of 1851. This sample was of the same specific gravity as the preparation mentioned in the London Pharmacopœia, and was practically the same preparation, but in witness's opinion the British Pharmacopœia entirely superseded all others, and all articles ordered in medicine should be prepared in accordance with its requirements. For instance, hydrocyanic acid (prussic acid) was double as strong in the London as in the British Pharmacopœia, and any chemist making up a prescription written with the intention of having the medicine made up according to the latter, might cause very grave results if he went by the former pharmacopœia.—The case was adjourned until June 1st, when Mr. Vaughan gave judgment as follows:—The summons against the defendant was for selling sal volatile which was deficient in alcohol and alkaline salt according to the acceptation of sal volatile as an article of commerce. Professor Redwood, both in his analysis and in the evidence he had given in this Court, distinctly stated that the article sold did not come up to the requirements of the British Pharmacopœia by one-half. This was not denied, and the next point to be considered was whether it was lawful to sell drugs prepared according to any other than the British Pharmacopœia. There really could be no question on this point, unless it was to be assumed that Acts of Parliament were to be entirely ignored, or taken as of no weight and non-existent. The evidence called for the defendant was simply that of the defendant himself, his manager, the wholesale chemist who supplied him, and the manufacturer. All these, he might say, were in the same boat, and he placed very little reliance on their testimony, for it seemed to him they were in ignorance of the Act of 1862. They might have acted on the knowledge which they previously possessed, but they did not themselves take the trouble to inquire into the present state of the law. He could not himself look at the Act without coming to the conclusion that any drug made up according to any other pharmacopœia than the Britannica was a violation of the Act; and in this view he was confirmed by the decision in the case of "*White v. Bywater*," wherein it was held that if a person asked for tincture of opium he was entitled to be supplied with it of the substance and quality mentioned in the British Pharmacopœia, and not with something of an inferior quality. The magistrate at Sheffield, in that case, at first dismissed the case, holding that in the absence of any special request for the drug according to the Pharmacopœia Britannica, the drug as described in other pharmacopœias could be sold. That was not the view taken by the Judges, who thought the magistrate ought to have convicted the defendant, and who sent the case back to him for re-hearing. He (Mr. Vaughan), therefore, could not entertain any doubt that the article in question must be held to have been not of the nature, substance, and quality of that demanded, and he was bound to convict. But, as he said before, if it could be proved that it was sold as it came from the wholesale manufacturer, he should hold it to be a case in which he could impose a nominal penalty. That had been proved, and he should act on his opinion. Before concluding, however, he hoped that this decision would have the effect of making all persons dealing in drugs remember that the provisions of the Act must be complied with, and that their drugs must be made up according to the British Pharmacopœia. He fined the defendant 40s. and 2s. cost of the summons.

### CORRESPONDENCE.

[*The Editor is not in any way responsible for opinions expressed by his correspondents.*]  
*To the Editor of the ANALYST.*

#### ABNORMAL BUTTER.

SIR,—Mr. Faber's recollection in connection with myself in the above matter is at fault.

It was distinctly understood that I was to be supplied with more complete details of analyses by Professor Stein, including fatty acids, soluble and insoluble, before I communicated my results to him, at that time a total stranger. I did not consider Professor Stein's Reichert results of any value.

Mr. Allen, though rather ungraciously, withdraws his extraordinary statement *re* Westphal, and I may therefore leave that subject. I may, however, draw attention to the fact that, with regard to the special butter, No. 402, Wigan, I was not the authority for the opinion expressed as to its adulteration, an opinion so ably dealt with upon theoretical grounds by Mr. Faber. The analyst for Wigan, and Dr. Jas. Bell, of Somerset House, had already certified the butter adulterated before I received my sample.

I shall be glad if you will find space for these few lines.—Yours,  
 Manchester, July 19th, 1889.

C. ESTCOURT.

### BOOKS RECEIVED.

COMMERCIAL ORGANIC ANALYSIS, VOLUME III., PART 1; ACID DERIVATIVES OF PHENOLS; AROMATIC ACIDS, TANNINS, DYES AND COLOURING MATTERS, BY ALFRED H. ALLEN, F.I.C., F.C.S.

# THE ANALYST.

AUGUST, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

### ON CONDENSED MILK AND THE ESTIMATION OF CASEIN AND LACTALBUMEN.

BY HARALD FABER.

(*Read at the Meeting, June, 1889.*)

Of the samples of condensed milk I have analysed, which are not many, two may be worthy of the attention of public analysts. One is a sample of a sweetened condensed milk, known generally as the "Goat Brand." It is said to be made from milk, from which "part of the cream" (or fat) has been abstracted. I bought it at 3½d. for a tin containing one pound, which is a lower price than that paid for condensed whole milk, but hardly a low price considering the quantity.

The composition was found to be—

|                   |    |    |    |       |           |
|-------------------|----|----|----|-------|-----------|
| Water             | .. | .. | .. | 30.91 | per cent. |
| Fat               | .. | .. | .. | 0.53  | "         |
| Total albuminoids | .. | .. | .. | 10.83 | "         |
| Milk sugar        | }  | .. | .. | 55.21 | "         |
| Cane sugar        |    | .. | .. |       |           |
| Ash               | .. | .. | .. | 2.52  | "         |

From this analysis, I think it may be calculated that the milk from which this condensed milk was made, contained about—

|             |    |    |    |      |           |
|-------------|----|----|----|------|-----------|
| Albuminoids | .. | .. | .. | 3.61 | per cent. |
| Fat         | .. | .. | .. | 0.18 | "         |
| Ash         | .. | .. | .. | 0.84 | "         |

or, that the milk was thoroughly skimmed on a mechanical cream-separator before being condensed, and it appears to me, that the public would better understand the quality of this kind of condensed milk, if it were called "condensed separated milk." An ordinary milk may be taken to contain at least 3.5 per cent. of fat, and it will be seen that there was left barely 5 per cent. of the original fat, or that the "part of the cream" abstracted amounts to over 95 per cent.

The other sample is an unsweetened milk, which, according to the label, is specially prepared for babies. In the directions for use, it is advised to dilute the milk with 7 parts of water for very young babies.

The composition of this milk was found to be—

|             |    |    |    |    |                 |
|-------------|----|----|----|----|-----------------|
| Water       | .. | .. | .. | .. | 77.51 per cent. |
| Fat         | .. | .. | .. | .. | 6.15 "          |
| Albuminoids | .. | .. | .. | .. | 5.35 "          |
| Sugar       | .. | .. | .. | .. | 9.55 "          |
| Ash         | .. | .. | .. | .. | 1.44 "          |

When this milk is diluted with 7 parts of water, the mixture will contain 2.8 per cent. of solids. To recommend such a mixture as the chief or only food for babies might easily have serious, if not fatal consequences.

Unsweetened condensed milk is used, to some extent, in the milk trade, when milk is scarce, in that way, that it is made up with water to its original volume, and no doubt frequently sold as new milk, probably mixed with some new milk. This is done to such an extent that a society of dairy farmers has expressed a wish to put a stop to it, and for that purpose has looked for a method to distinguish between fresh milk and milk which has been condensed and afterwards diluted with water.

Milk contains a genuine albumen, lactalbumen, which, like other albumens, is coagulated when its watery solution is heated to a certain temperature, varying according to circumstances. The more salt the solution contains the higher is the temperature of coagulation, while acids in small amounts lower it. It therefore at once suggests itself that the heating necessary for condensing milk, and especially for sterilising the milk after the closing of the tins, will coagulate the lactalbumen, which is thereby rendered insoluble in water, and that this change in the milk would enable one to distinguish between fresh milk and milk which has been condensed. But, on the other hand, it is generally held, that for some reason or other lactalbumen in the milk is not coagulated when milk is boiled, and, as is a well-known fact, there is no precipitation of coagulated albumen in boiled milk. Some analyses and remarks made a few years back by Professor Hammarsten, to whom, and his pupils, we owe most of our knowledge of the albuminoids in milk, seem to show that the lactalbumen in milk is really altered in boiled, and is at least partly coagulated. As a method was wanted for distinguishing between fresh and condensed milk, I made a few experiments to find whether, and how far, the albumen was coagulated by heating milk, and whether it was possible by analysis to demonstrate such coagulation.

In order to be able to do this, it is necessary to use very exact methods for separating casein and lactalbumen. Concerning the complete precipitation of casein in milk, I think I can do no better than quote from a very exhaustive and exact publication on "The Analytical Estimation of the Albuminoids, with Special Reference to Milk," by John Sebelien, Professor at the Agricultural College at Aas, in Norway, which appeared last year in the transactions of the Royal Academy of Science at Copenhagen:—

"The method of estimating casein in milk first used by Millon and Commaille, and further developed by Hoppe-Seyler, to precipitate it by means of dilute acetic acid in milk diluted with a certain quantity of water, can never give exact results, as the casein is far from completely precipitated by this reagent. The same may be said of sulphuric acid as used by Frenzel and Weyl. Still less exact is the method proposed by Manetti and Musso, to precipitate by rennet.

"A better method is the precipitation by means of sulphate of magnesia, which was perhaps first used by Mitscherlich in 1847, and which, with different modifications, has been adopted by Tolmatscheff, Makris, and Hoppe-Seyler."

Sebelien has made some experiments to ascertain how far sulphate of magnesia, and the equally effective chloride of sodium (which, however, for this purpose must contain some chloride of calcium), give a complete precipitation of casein. He prepared some pure casein according to Hammarsten's method, viz.:—Milk is diluted with about five volumes of water, so much dilute acetic acid is added that the mixture contains a little less than 0.1 per cent. of acetic acid. The casein is precipitated and sinks to the bottom, it is washed by decantation, filtered off, dissolved in as little soda as possible, filtered to get rid of the fat globules, precipitated again by acetic acid, washed, filtered off, again dissolved in very little soda, and so on. The third precipitation is pressed between filter-paper, ground in a mortar with strong alcohol, until it forms a very fine emulsion, then quickly filtered, washed with strong alcohol and afterwards with ether, pressed between filter-paper and ground in a mortar, stirring repeatedly while the ether evaporates. It is finally dried over sulphuric acid, and is then a snowy white very fine powder, which will stand heating to 100° C. in an air bath. It is completely soluble in alkalis, their carbonates and phosphates, in lime—and baryta-water, and even in water in which is stirred up a fine powder of the carbonates of lime, baryta, or magnesia. When the casein is dissolved in a very dilute solution of phosphate of soda, and small quantities of a solution of chloride of calcium is afterwards added, the clear solutions will turn white and milky, looking exactly like skim-milk, and containing the casein in the same state in which it is present in milk, but no trace of other organic matter. Such a solution of casein forms even a skin on top when boiled.

On solutions of pure casein made in this way Sebelien made some experiments. He ascertained the amount of casein in the solution by estimating the nitrogen both in the solution and in the precipitate formed by tannic acid, which he has shown will completely precipitate all the albuminoids of the milk. He then precipitated the casein by sulphate of magnesia and by chloride of sodium—by first adding two volumes of a saturated solution of the salts and then so much of the pulverised crystals of the salts as can be taken up in solution (it is very essential that the solution is completely saturated with the salts). The completeness of the precipitation of the casein was proved, not only by the amount of nitrogen in the precipitate, but by the almost complete absence of any nitrogenous precipitate by tannic acid in the diluted filtrate.

As milk contains a trace of globuline, which is not precipitated by chloride of sodium, but by sulphate of magnesia, and as the precipitates by sulphates of magnesia are more easily treated by the Kjeldahl method, this salt is here to be preferred.

In order to try whether this effective method of precipitating the casein will allow of a correct estimation of the albumen in the filtrate, Sebelien made some experiments on mixtures of solutions of pure casein and pure lactalbumen. Pure lactalbumen may be prepared, according to Sebelien (1885) as follows:—

To the filtrate from the precipitation by sulphate of magnesia of casein in milk (which filtrate is a concentrated solution of sulphate of magnesia), acetic acid is added so as to give  $\frac{1}{4}$  per cent. of acetic acid in the solution. The lactalbumen is thereby precipitated; it is



filtered off, pressed between filter-paper, stirred up in water (together with the filter-paper), and the water exactly neutralised. The lactalbumen is hereby dissolved. The solution of lactalbumen is filtered off, again saturated with sulphate of magnesia, filtered and precipitated by  $\frac{1}{4}$  per cent. of acetic acid. The precipitate is filtered off, dissolved and dialysed, to remove the salt. The solution thus prepared can be used immediately, or the lactalbumen may be prepared as a powder for future use. In order to do this, the solution is precipitated by alcohol, filtered, washed by alcohol and ether, and ground in alcohol, etc., like the treatment of the casein; it is in this way obtained as a fine white powder, completely soluble in water. It will always retain a trace of the salt, but this will not interfere with the experiments.

Having prepared a milky solution of pure caseine and a solution of pure lactalbumen, and having estimated the nitrogen in both, Sebelien mixed known quantities of the two solutions and analysed the mixture by the following method:—Precipitating the caseine by sulphate of magnesia, washing with a concentrated solution of this salt until the filtrate contained no albumen, then precipitating the albumen in the filtrate after dilution with water, by means of tannic acid or phosphortungstic acid. In these precipitates the nitrogen was estimated (all estimations of nitrogen by Kjeldahl's method) f. inst.

I.—4.180 grms. of a solution of caseine contained 0.01862 grm. N. or 0.445 per cent.

5.742 grms. of a solution of lactalbumen contained 0.01316 grm. N. or 0.229 per cent.

20 c.c. caseine solution was mixed with 30 c.c. lactalbumen solution; this mixed solution contains 0.316 per cent. nitrogen, viz., 0.174 per cent. "caseine N." and 0.138 per cent. "albumen N."

1.—10.125 grms. of the solution gave in the precipitate by  $\text{Mg SO}_4$

0.01876 grm. N. = 0.185 caseine N.

In the filtrate, tannic acid precipitated,

0.01428 grm. N. = 0.142 albumen N.

Total .. 0.327 N.

2.—10.180 grms. of the same solution gave in the precipitate by  $\text{Mg SO}_4$

0.01750 grm. N. or 0.172 p.c. caseine N.

In the filtrate, tannic acid precipitated,

0.0154 grm. N. or 0.151 p.c. albumen N.

Total .. 0.323 p.c. N.

II.—4.862 grms. of a solution of casein contained 0.01610 grm. N. or 0.331 per cent.

10.193 grms. of a solution of lactalbumen contained 0.00686 grm. N. or 0.067 per cent.

Equal volumes of these solutions were mixed, giving a solution containing 0.200 per cent. N., of which 0.166 per cent. was derived from the caseine and 0.034 per cent. from the lactalbumen.

9.780 grms. of this solution gave a precipitate by  $\text{Mg. SO}_4$ , containing

0.01568 grm. N. s. 0.160 p.c. caseine N.

In the filtrate, phosphortungstic acid gave a precipitate containing

0.0042 grm. N. or 0.043 p.c. albumen N.

Total .. 0.203 p.c. N.

"The separation of the two albuminoids is as complete as possible, and the

amounts found by analysis agree with the amounts calculated as closely as could be expected by an ordinary quantitative analysis."

I have estimated the albumen in some samples of milk by this method, and made some experiments with milk by heating it to different temperatures, in order to find whether the lactalbumen was coagulated, and I found that heating milk to 75° C. will, even in neutral (or amphoteric) milk, considerably decrease the amount of lactalbumen found. This must evidently be explained in this way, that the lactalbumen, which is coagulated, although it does not form lumps and sink to the bottom, still is in such a modification that it will be carried down by the casein when this is precipitated, and, therefore, escape estimation as lactalbumen.

The amount of lactalbumen found in fresh milk may vary between 0.35 and 0.45 per cent., and perhaps reach still higher amounts, *f. inst.*, probably in Jersey milk. In boiled milk I found that about the two-thirds of the albumen was coagulated. In the above-mentioned "Goat Brand" sweetened condensed milk, which was slightly sour when opened, and, therefore, most likely was so when filled in the tin, the total albuminoids were 10.83 per cent., of which only 0.085 was soluble albumen, a much lower amount than I have found in boiled and condensed milk which was not acid.

I have analysed an unsweetened condensed milk, known as "The First Swiss Brand," with the following result:—

|                 |    |    |    |    |    |                       |
|-----------------|----|----|----|----|----|-----------------------|
| Water           | .. | .. | .. | .. | .. | 62.97 per cent.       |
| Fat             | .. | .. | .. | .. | .. | 10.67 "               |
| Casein*         | .. | .. | .. | .. | .. | 9.236 "               |
| Soluble Albumen | .. | .. | .. | .. | .. | 0.324 "               |
| Sugar..         | .. | .. | .. | .. | .. | 14.55 (by difference) |
| Alb. ..         | .. | .. | .. | .. | .. | 2.25 per cent.        |

This milk is evidently condensed to about one-third of its original bulk, which would give these amounts of caseine and soluble albumen in the original milk:—

|              |    |    |    |    |    |                |
|--------------|----|----|----|----|----|----------------|
| Caseine      | .. | .. | .. | .. | .. | 3.08 per cent. |
| Sol. albumen | .. | .. | .. | .. | .. | 0.11 "         |

I ought to mention that this estimation of albumen was made by boiling the filtrate from the precipitation of the caseine, a method which is not so exact as the precipitations by tannic acid or phosphotungstic acid, as, according to Sebelien's experiments, as much as 12 per cent. of the albumen may remain unprecipitated; still, it is sufficiently exact to show that the milk has been heated, and, therefore, is not "fresh milk."

The low percentage of soluble albumen, if estimated by a sufficiently exact method, will, according to my experience, be a reliable indication, that milk has been heated to at least 75° C., and, as all condensed milk must be heated to at least that temperature to ensure its safe keeping, chemical analysis will be able to prove that such milk is not fresh.

#### DISCUSSION.

Mr. ALLEN said the paper suggested one point which was a crying scandal, and that was the false and misleading statements made on the labels of some brands of condensed milk. The directions frequently were to dilute the condensed milk with five, six, and even eight times its measure of water, when, as a fact, the milk had only been

\* Containing the coagulated albumen.

concentrated to about one-third of its original bulk. The consequence was that if the milk was diluted to the extent directed, and a child were given the amount which would be sufficient in the case of uncondensed milk, it would be half starved. He thought they should not allow these false statements and misleading directions to go unchallenged. Of course, if a case were taken into Court there was the objection that the retailer who sold the can of condensed milk was not the real author of the fraud, but ultimately the offence would come home to the manufacturer, who would find an effect on his trade; and certainly the public ought to be made aware that certain brands of condensed milk are not what they profess to be.

Dr. VIETH said their best thanks were certainly due to Mr. Faber for the paper he had brought before them. They ought to congratulate themselves on the opportunity of reading in *THE ANALYST* the very interesting and important experiments of a foreign chemist which Mr. Faber had included in his paper, experiments which originally had been published in a language with which only very few among them were familiar. With regard to the point raised by Mr. Allen, he was of opinion that the total proteids formed the best gauge by which the degree of evaporation could be judged, the proteids being pretty constant and amounting to about 3.5 per cent. As to the mode of distinguishing between fresh milk and milk which had been heated for this really was the point under discussion—he was of opinion that the determination of the albumen was not a suitable method. Not only was the quantity of albumen present in fresh milk very small, but the separation of the various nitrogenous bodies seemed difficult and uncertain, and the method proposed rather cumbersome. A very simple test for distinguishing between fresh and scalded milk, proposed years ago, consists in adding tincture of guaiacum, which gives a blue colour with fresh, but not with boiled milk. The reaction used to be explained by the presence of ozone in fresh milk, but Babcock, in a recent publication, ascribes it to the presence of fibrine.

Mr. STOKES said that having tried various methods for complete analysis, he found none that constantly summed up to 100 on addition of the constituents. He noticed the same fact in all the complete analyses published hitherto.

In regard to erroneous labelling of tins, he was afraid that no conviction would be obtained. Even in the case of a considerable number of samples prosecuted on his analysis for deficiency of fat, the magistrate held that the samples having come into the possession of the vendors soldered down, so that they could not have tampered with them, no action could lie against the vendors.

The distinction between condensed and fresh milk by means of guaiacum depended upon the milk having been boiled or not. Mr. Stokes, having had charge of, and having practically worked, a vacuum-condenser, knew that often milk was condensed at a temperature not higher than when it left the cow, from 90° to 100° F.; hence the guaiacum test would in such cases fail.

Dr. VOELCKER asked Mr. Faber whether he had examined any considerable number of samples of condensed milk, and if so, whether he had found each kind to be uniform in composition. In analysing a large number of one particular brand a few years ago he (Dr. Voelcker) had found great variation in different samples. He understood that for infant life especially, it was important, not only to see that sufficient food constituents were supplied when the milk was diluted, but also that the composition should be always alike.

Mr. ADAMS said he quite agreed with Mr. Allen and Mr. Hehner as to the importance of not overlooking the constitution of these milks, because there was a point which had escaped remark, and that was the presence or absence of fat, a substance most necessary as a digestive agent. It was by means of the animal fat that true chyle was produced, and the albuminoids were got into the lacteals. He was convinced that a milk

which had a constitution like the first of those given must be a most indigestible substance to give any animal, more especially an infant, and that was a reason why the true facts should be widely known.

With regard to cane sugar in abundance, he considered it, from a medical point of view, to be injurious. Cane sugar was not easily digested, at all events by young creatures. Of all sources of complaints and disease, a very frequent one was the habit of giving children so many lollipops, and therefore he thought, in the custom of adding sugar, there was injury to the public in being misled as to the extent of dilution these milks will bear. A child must simply starve if fed on such a milk as the first one, especially if diluted to seven times its bulk. Animal fat was a most important food—in one sense more even than the albuminoids, for without fat the albuminoids could not be so well turned to their proper account.

With regard to prosecutions under the Food and Drugs Act, it was a difficult point, no doubt; but he should think there was no doubt that a case of that kind could be dealt with by the law courts.

Mr. ALLEN asked if a person could be convicted of selling a condensed milk when he had no hand at all in its preparation, and palpably so.

Mr. ADAMS said it was similar to pickles and green peas, in which cases they had no difficulty in obtaining convictions. He did not see that that ought to be a great obstacle.

Mr. STOKES said the peas contained an article injurious to health.

Mr. FAHER, in reply, said, that with regard to estimating soluble albumen, there was no difficulty when the amount was about 0·3 or 0·4 per cent., and if the amount of soluble albumen was so small as to be difficult to estimate, that was by itself a proof that the milk had been heated.

As to the presence of fibrine in milk, he was very doubtful whether that statement would be found correct after further investigation.

In reference to Mr. Stokes' remarks concerning the temperature of milk during condensation, it was quite certain you could condense milk at a low temperature, but in any case would the milk have to be heated after the closing of the tins to such a degree that the albumen was coagulated in order to sterilize the milk, and thereby ensure its keeping for any length of time?

He only knew of very few analyses by this method, as it was comparatively new.

## ON THE QUANTITY OF VOLATILE ACIDS PRESENT IN BUTTER-FAT.

By DR. P. VIETH.

*(Read at the Meeting, June, 1889.)*

THE more precise title of my paper would be "On that quantity of volatile acids present in butter-fat which is determined when butter-fat is examined according to Reichert-Wollny's method." The results obtained find expression in the number of cubic-centimetres of deci-normal alkali required for neutralising the volatile and, in water, soluble acids.

When Dr. Wollny, in 1887, published his modification of the Reichert-Meissl method for the examination of butter-fat, I in common, I believe, with a great many analysts, cherished the hope that the method would turn out an extremely useful one. Avoiding outside influences, which might interfere with the process, seemed to insure correctness, and working according to fixed and widely adopted rules, promised uniformity of results. The modified method, then, seemed to be well suited for the examination of butter-fat and the detection and quantitative determination of admixed

foreign fat, provided the volatile acids present in genuine butter-fat of any origin varied within not too wide limits. According to our experience at the time, we assumed that the volatile acids yielded by 5 grms. pure butter-fat required for neutralisation from 25 to 30 c.c. deci-normal alkali solution. Since then we have learned that those limits were drawn far too narrow, that genuine butters are not unfrequently met with giving results which fall outside, more particularly below, the said limits. The more the matter is investigated, the more cases of undoubtedly genuine butter-fat containing abnormally small amounts of volatile acids are observed.

My own experience with Wollny's modification of Reichert's method commences with a sample of butter-fat sent from Kiel to the members of the "International Committee," formed to investigate into the question of butter-fat analysis. I examined this sample on October 20th (a) of last year, and again on January 17th (b) and May 2nd (c) of the present year, with the following results:—

No. 1. Butter-fat from Kiel (a) 31·8, 31·6, 31·8, 31·9, 31·9.  
(b) 32·1.  
(c) 32·1.

The insoluble acids in this sample amounted to 87·04 per cent.

The agreement between the results obtained at the various occasions is satisfactory, a fact on which I wish to lay some stress, because not only was, on the several occasions, a fresh soda solution used for saponification and a fresh baryta solution for titration, but also the distilling apparatus employed for the earlier experiments had to be replaced by another one, which was of somewhat different dimensions.

During the time from the middle of November to the middle of June, I applied Wollny's method in the examination of 63 samples of butter as sold in the London market. The results were as follows:—

#### FRENCH BUTTER.

| No. | Date.      |      | No. | Date.     |      | No. | Date.     |      |
|-----|------------|------|-----|-----------|------|-----|-----------|------|
| 2.  | 14. 11. 88 | 26·3 | 12. | 23. 1. 89 | 28·5 | 22. | 27. 3. 89 | 29·0 |
| 3.  | 23. "      | 27·2 | 13. | 31. "     | 27·7 | 23. | 4. 4. 89  | 29·8 |
| 4.  | 28. "      | 27·4 | 14. | 6. 2. 89  | 28·8 | 24. | 9. "      | 30·5 |
| 5.  | 6. 12. 88  | 26·8 | 15. | 14. "     | 29·2 | 25. | 16. "     | 29·2 |
| 6.  | 13. "      | 27·6 | 16. | 20. "     | 29·1 | 26. | 9. 5. 89  | 30·6 |
| 7.  | 20. "      | 26·1 | 17. | 22. "     | 26·4 | 27. | 14. "     | 30·1 |
| 8.  | 28. "      | 26·1 | 18. | 26. "     | 27·5 | 28. | 28. "     | 29·8 |
| 9.  | 3. 1. 89   | 26·7 | 19. | 6. 3. 89  | 29·2 | 29. | 4. 6. 89  | 30·6 |
| 10. | 10. "      | 27·0 | 20. | 13. "     | 28·7 | 30. | 11. "     | 29·9 |
| 11. | 17. "      | 27·5 | 21. | 21. "     | 29·5 |     |           |      |

#### SWEDISH BUTTER.

| No. | Date.      |      | No. | Date.     |      | No. | Date.     |      |
|-----|------------|------|-----|-----------|------|-----|-----------|------|
| 31. | 14. 11. 88 | 27·6 | 39. | 10. 1. 89 | 27·6 | 46. | 6. 3. 89  | 27·2 |
| 32. | 23. "      | 28·2 | 40. | 17. "     | 28·6 | 47. | 13. "     | 28·4 |
| 33. | 28. "      | 27·6 | 41. | 23. "     | 27·4 | 48. | 21. "     | 28·1 |
| 34. | 6. 12. 88  | 29·3 | 42. | 31. "     | 28·2 | 49. | 9. 4. 89  | 28·2 |
| 35. | 13. "      | 29·0 | 43. | 6. 2. 89  | 29·4 | 50. | 16. "     | 28·5 |
| 36. | 20. "      | 28·7 | 44. | 14. "     | 28·2 | 51. | 14. 5. 89 | 26·9 |
| 37. | 28. "      | 27·8 | 45. | 26. "     | 29·1 | 52. | 22. "     | 29·3 |
| 38. | 3. 1. 89   | 28·2 |     |           |      |     |           |      |

#### KIEL BUTTER.

| No. | Date.     |      | No. | Date.     |      | No. | Date.     |      |
|-----|-----------|------|-----|-----------|------|-----|-----------|------|
| 53. | 15. 5. 89 | 29·1 | 55. | 28. 5. 89 | 27·3 | 57. | 11. 6. 89 | 27·4 |
| 54. | 22. "     | 27·8 | 56. | 4. 6. 89  | 28·7 |     |           |      |

## BUTTER MANUFACTURED IN LONDON.

| No. | Date.     |      | No. | Date.     |      | No. | Date.    |      |
|-----|-----------|------|-----|-----------|------|-----|----------|------|
| 58. | 27. 3. 89 | 29.2 | 61. | 30. 4. 89 | 27.6 | 63. | 7. 5. 89 | 28.7 |
| 59. | 29. „     | 29.2 | 62. | 7. 4. 89  | 28.6 | 64. | 22. „    | 28.3 |
| 60. | 30. 4. 89 | 28.1 |     |           |      |     |          |      |

With the exception of the butter manufactured in London, which was churned on the premises of the Aylesbury Dairy Company, in Bayswater, little is known as to origin and history of the foregoing samples. The results must all be considered as quite normal.

The samples, of which I shall have to speak in what follows, do not refer to butter manufactured for sale. They were, moreover, prepared from small quantities of milk or cream in the laboratory under my continuous superintendence, and with exclusion of every possibility of any admixture of foreign fat taking place. The mode of proceeding was as follows:—One gallon of milk was set in a shallow pan, kept under lock for twenty-four hours, the cream taken off and churned, the butter melted, and the fat filtered. All the samples form part of a systematic investigation, which was commenced early in February and continued till the middle of May, and in one direction is still proceeding.

At the end of January a brother analyst asked me for two samples of butter of undoubted genuineness. In order to put the purity entirely beyond doubt, I had two samples of cream churned into butter by shaking the cream in glass bottles. Part of the butter thus prepared I kept for examination. The one sample referred to cream produced at a butter-factory situated in Sussex; the volatile acids in the butter-fat were found to be normal. The other sample referred to cream separated on the Aylesbury Dairy Company's Farm, near Horsham, from milk produced by cows kept on the estate; the composition of the butter-fat was to my greatest surprise quite abnormal. I determined at once to try to find out the cause for this abnormal state of affairs, and also to see whether anything similar existed with regard to milk produced on other farms at that time.

First of all, another sample of cream from the butter-factory in Sussex was examined. The two samples gave the following results:—

| No. |                        | Date.    |            |
|-----|------------------------|----------|------------|
| 65. | Cream from Gl., Sussex | 2. 2. 89 | 29.8       |
| 66. | „ „                    | 18. „    | 28.8, 28.3 |

I next had small quantities of butter prepared from samples of milk received from thirty-five farms supplying the Aylesbury Dairy Company at the time. The results were as follows:—

| No. |           | Date.     |           |           |            |
|-----|-----------|-----------|-----------|-----------|------------|
| 67. | P.M. Milk | 19. 2. 89 | from St., | Wiltshire | 27.8       |
| 68. | „         | 19. 2. 89 | „ He.,    | „         | 28.1       |
| 69. | „         | 19. 2. 89 | „ Fa.,    | „         | 30.9       |
| 70. | „         | 26. 2. 89 | „ Wh. R., | „         | 30.4       |
| 71. | „         | 26. 2. 89 | „ Ru.,    | „         | 27.9       |
| 72. | „         | 26. 2. 89 | „ Sm.,    | „         | 24.7, 24.8 |
| 73. | „         | 27. 2. 89 | „ Bo.,    | „         | 24.2, 23.9 |
| 74. | „         | 27. 2. 89 | „ Hw.,    | „         | 28.7       |
| 75. | „         | 27. 2. 89 | „ Da.,    | „         | 26.7       |
| 76. | „         | 27. 2. 89 | „ Ke.,    | „         | 25.6       |

| No.  |           | Date.     |      |          |                 |            |
|------|-----------|-----------|------|----------|-----------------|------------|
| 77.  | P.M. Milk | 28. 2. 89 | from | Be.,     | Wiltshire       | 29.9       |
| 78.  | "         | 28. 2. 89 | "    | Po. J.,  | "               | 32.4, 31.8 |
| 79.  | "         | 1. 3. 89  | "    | Cr.,     | "               | 26.5       |
| 80.  | "         | 1. 3. 89  | "    | Gr.,     | "               | 26.2       |
| 81.  | "         | 1. 3. 89  | "    | Hi.,     | "               | 25.8       |
| 82.  | "         | 3. 3. 89  | "    | Go.,     | "               | 29.1       |
| 83.  | "         | 3. 3. 89  | "    | Wo.,     | "               | 25.2       |
| 84.  | "         | 4. 3. 89  | "    | Ms.,     | "               | 26.8       |
| 85.  | "         | 4. 3. 89  | "    | Po. R.,  | "               | 28.1       |
| 86.  | "         | 4. 3. 89  | "    | Po. S.,  | "               | 26.6       |
| 87.  | "         | 6. 3. 89  | "    | Mg.,     | "               | 27.2       |
| 88.  | "         | 6. 3. 89  | "    | Kv. Fr., | "               | 25.5       |
| 89.  | "         | 6. 3. 89  | "    | Kv. Sh., | "               | 31.4       |
| 90.  | "         | 19. 2. 89 | "    | Ph.,     | Berkshire       | 30.8, 30.4 |
| 91.  | "         | 26. 2. 89 | "    | Kv.,     | "               | 28.2       |
| 92.  | "         | 28. 2. 89 | "    | Re.,     | "               | 28.0       |
| 93.  | "         | 1. 3. 89  | "    | Wh. R.,  | "               | 29.5       |
| 94.  | "         | 3. 3. 89  | "    | Je.,     | "               | 27.4       |
| 95.  | "         | 4. 3. 89  | "    | Bu.,     | "               | 27.2       |
| 96.  | "         | 3. 3. 89  | "    | By.,     | Cheshire        | 28.0       |
| 97.  | "         | 5. 3. 89  | "    | Du.,     | "               | 28.2       |
| 98.  | "         | 28. 2. 89 | "    | Ho.,     | Oxfordshire     | 26.9       |
| 99.  | "         | 5. 3. 89  | "    | El.,     | "               | 27.5       |
| 100. | "         | 5. 3. 89  | "    | Ta.,     | Gloucestershire | 25.7       |
| 101. | "         | 5. 3. 89  | "    | Hd.,     | Warwickshire    | 27.2       |

It will be seen that in two instances the results fell below 25; the lowest and highest figures observed were 23.9 and 32.4 respectively.

I now come to the samples having an abnormal composition. As mentioned before, the milk from which the butter-fat in question was abstracted, was produced by cows kept on the Aylesbury Dairy Company's estate near Horsham. The following were the first results obtained :—

| No.  |                    | Date.  |    |            |
|------|--------------------|--------|----|------------|
| 102. | Cream from Horsham | 2.2.89 | .. | 20.9, 21.2 |
| 103. | "                  | 9.     | .. | 21.4, 21.2 |
| 104. | "                  | 15.    | .. | 20.4.      |

The herd which produced the milk consisted at the time of sixty head of cattle, viz., thirty-nine Shorthorn, sixteen Kerry, and five Jersey cows. In order to ascertain whether the breed had anything to do with the abnormal composition of the butter-fat, samples of Shorthorn, Kerry, and Jersey milk were examined separately. The first three samples did not show any striking difference to exist between the three breeds (see the following table), and another point was therefore taken into consideration, viz., the food.

The diet of the cows consisted of suitable quantities of hay, brewers' grains, and linseed—feeding materials which enjoy a very wide application; further, of silage, on average four pounds per head per day; and oatmeal, on average six pounds per head per day. The effect of the two last-named constituents of the diet seemed to me to require elucidation; first, because silage has only since the last few years entered the list of feeding-stuffs for farm live stock; and, second, because the ration of oatmeal is much higher than usually given. After February 18th the Jerseys, and after February

25th the Kerrys ceased to receive silage in their food, while it was always given to the Shorthorns. The results contained in the table prove that withholding the silage had no marked effect on the composition of the butter-fat. After March 16th silage was given again to all the cows, but the six pounds of oat-meal were replaced by one pound of barley-meal, two pounds of wheat-meal, and three pounds of linseed cake. From this time the percentage of volatile acids gradually increased, and on the 29th April could be considered normal in the cases of the three breeds, although approaching the lower limit in two cases:—

| No.           | Material.                             | Shorthorns. | Kerry's.   | Jerseys.   |
|---------------|---------------------------------------|-------------|------------|------------|
| 105, 106, 107 | P.M. Milk, 17. and A.M. Milk, 18.2.89 | 21.4        | 22.5       | 20.3       |
| 108, 109, 110 | " " 24. " " 25.2.89                   | 22.0        | 23.9       | 21.4       |
| 111, 112,     | " " 3. " " 4.3.89                     | 22.8        | 23.1       | *          |
| 113, 114, 115 | " " 10, " " 11.3.89                   | 21.8        | 23.1       | 21.6       |
| 116, 117, 118 | " " 24. " " 25.3.89                   | 23.5        | 24.8       | 23.3       |
| 119, 120, 121 | " " 31.3 " " 1.4.89                   | 24.0        | 26.0, 26.5 | 23.6, 24.1 |
| 122, 123, 124 | " " 28. " " 29.4.89                   | 25.3        | 26.1       | 27.2       |
| 125, 126, 127 | " " 12. " " 13.5.89                   | 25.8, 25.9  | 28.6, 28.6 | 27.1, 27.2 |

\* Sample lost.

After May 13th no more separate samples of the three breeds were taken, but one sample of cream from the mixed milk of the herd was examined weekly, and I purpose continuing doing so for at least one year. The following results have been obtained up to the present:—

| No.                       | Date.   |      |
|---------------------------|---------|------|
| 128. Cream from Horsham.. | 21.5.89 | 26.2 |
| 129. " " ..               | 27.5.89 | 26.8 |
| 130. " " ..               | 4.6.89  | 26.8 |
| 131. " " ..               | 11.6.89 | 26.2 |

One might naturally feel inclined to put the improvement which took place after March 16th on account of the abandonment of the large ration of oatmeal, and expect a further increase in the percentage of volatile acids by giving up feeding cereals altogether. To put this to the test, four Shorthorn cows were fed on a diet containing neither oats, nor barley, nor wheat from April 8th to May 2nd; after the latter date they received six pounds of oatmeal per head per day. The results were as follows:—

FOOD CONTAINING 1 lb. BARLEY AND 2 lbs. WHEAT.

|          |                                   |    |            |
|----------|-----------------------------------|----|------------|
| No. 132. | P.M. Milk 7. and A.M. Milk 8.4.89 | .. | 26.0, 26.1 |
|----------|-----------------------------------|----|------------|

FOOD CONTAINING NO CEREALS.

|          |                                     |    |            |
|----------|-------------------------------------|----|------------|
| No. 133. | P.M. Milk 14. and A.M. Milk 15.4.89 | .. | 24.4, 24.2 |
| " 134.   | " 22. " 23.4.89                     | .. | 24.7       |
| " 135.   | " 28. " 29.4.89                     | .. | 24.9       |

FOOD CONTAINING 6 lbs. OATS.

|          |                                     |    |            |
|----------|-------------------------------------|----|------------|
| No. 136. | P.M. Milk 12. and A.M. Milk 13.5.89 | .. | 26.0, 26.0 |
|----------|-------------------------------------|----|------------|

The results show that neither barley and wheat nor oats have an unfavourable effect on the composition of butter-fat; on the contrary, in these experiments the volatile acids decreased when no cereals were given, and increased after oats had entered



into the diet. The variations, however, were hardly large enough to allow any definite conclusions to be drawn from them.

It has been found by several investigators, and also published, that the butter-fat contained in the milk of stale cows, *i.e.*, cows which are approaching the end of the period of lactation, is remarkable for the low percentage of volatile acids which it contains. My own experience on this point is as follows:—

|  |                                       |    |      |  |
|--|---------------------------------------|----|------|--|
| SHORTHORN COW, CALVED 31. 1. 89.         |                                       |    |      |  |
| No. 137.                                 | P.M. Milk 18. and A.M. Milk 19. 2. 89 | .. | 25.1 |  |
| SHORTHORN COW, CALVED 16. 5. 88.         |                                       |    |      |  |
| No. 138.                                 | P.M. Milk 18. and A.M. Milk 19. 2. 89 | .. | 18.6 |  |
| " 139.                                   | " 21. 2. 89                           | .. | 17.6 |  |
| " 140.                                   | A.M. Milk 22. 2. 89                   | .. | 17.7 |  |
| for ten days' food containing no silage. |                                       |    |      |  |
| " 141.                                   | P.M. Milk 13. and A.M. Milk 14. 3. 89 | .. | 17.9 |  |
| SHORTHORN COW, CALVED 6. 1. 88.          |                                       |    |      |  |
| No. 142.                                 | P.M. Milk 21. 2. 89                   | .. | 15.0 |  |
| " 143.                                   | A.M. Milk 22. 2. 89                   | .. | 16.0 |  |
| " 144.                                   | P.M. Milk 1. and A.M. Milk 2. 3. 89   | .. | 16.3 |  |
| for ten days' food containing no silage. |                                       |    |      |  |
| " 145.                                   | P.M. Milk 13. and A.M. Milk 14. 3. 89 | .. | 14.7 |  |

The two stale cows gave exceedingly low results, more especially the second one, which, at the time of taking the last sample, had calved sixty-two weeks previously. Sample No. 144 contained 91.28 per cent. insoluble fatty acids.

It remains to be seen whether the low results obtained in February and March cannot be traced to the fact that the cows were then much advanced in the period of lactation. I have calculated the average time elapsed since calving with respect to all the samples, but do not intend troubling you with all the details. The few instances given hereafter will serve as examples, and at the same time prove that, taking into consideration the time elapsed since calving, does not suffice to explain the low percentages of volatile acids found.

| No. of Experiment. | Number and Breed of Cows. |            |       | Weeks Elapsed since Calving. | Result of Butter-fat Examination. |
|--------------------|---------------------------|------------|-------|------------------------------|-----------------------------------|
| { 123              | 18                        | Kerrys     | .. .. | 18                           | 26.1                              |
| { 120              | 16                        | "          | .. .. | 27                           | 26.25                             |
| { 106              | 16                        | "          | .. .. | 26                           | 22.5                              |
| { 120              | 16                        | "          | .. .. | 27                           | 26.25                             |
| { 122              | 43                        | Shorthorns | .. .. | 29                           | 25.3                              |
| { 105              | 38                        | "          | .. .. | 30                           | 21.4                              |
| { 121              | 5                         | Jerseys    | .. .. | 40                           | 23.85                             |
| { 107              | 5                         | "          | .. .. | 40                           | 20.3                              |

In the examples given, we have in the first and second instance a difference in the times elapsed since calving, but closely agreeing results; in the third and fourth, fifth and sixth, seventh and eighth instances, on the other hand, the times elapsed since calving agree, and the quantities of volatile acids differ.

I have failed, then, to bring home to a certain cause the abnormal composition of the butter-fat produced during the months of February, March, and part of April, and as I do not intend to leave the firm ground of experimental proof, must abstain from entering into speculation on possibilities and probabilities.

## DISCUSSION.

Mr. FABER said it was a consolation, when so low results were found in butter fat from cows, to be told that one of them had been in milk for 62 weeks. Of course he took it that that cow did not give very much milk, and it was not a usual thing in dairy-farming to keep a cow so long in milk, and, therefore, he did not think so low results as these from single cows would ever be found in commercial butter. Of course it was of great interest to find how low an amount of volatile acids could be obtained, and Dr. Vieth had rendered valuable service by these analyses; but he hoped these results would not be used to lower still further the figure for calculation which they would have to apply to commercial butter.

Mr. ALLEN asked if Dr. Vieth had made any determinations of the soluble or insoluble acids as well as of the volatile acids, because there should be a certain relation between them, and it would be interesting to know if that occurred in these cases of abnormal butters.

Dr. VIETH, in reply, said he had given the result of a very stale cow as being particularly interesting. When results as low as 20 were found in milk from a herd of 60 cows of different breeds, it was a very natural question what would be the limits when the average was so low. In a herd of cows there must be some individuals giving high and some giving low results, and with this point in view he analysed these stale and newly-calved cows. He was rather glad to find this exceptionally stale cow, as it was interesting to see how low the results may fall.

In reply to Mr. Allen, Dr. Vieth said he had made no determinations of the insoluble and the total soluble acids, for the simple reason that he had not the time to do it. He made two preliminary experiments with a view to determine the volatile soluble and volatile insoluble acids, hoping there might be something in it, but the results were so discouraging that he gave it up in despair.

He might mention incidentally that the flasks which he used for the saponification and distillation lost weight at a very uniform rate, the loss on each occasion amounting to from five to eight milligrams.

*(Conclusion of the Society's Proceedings)*

## NOTE ON A RECENT PAPER BY DR. JOHNSTONE.

By H. DROOP RICHMOND.

At the end of his paper (ANALYST XIV. 113), entitled "The Estimation of Soluble and Insoluble Fatty Acids in Butter," Dr. Johnstone gives some equations to represent the action between caustic potash and glycerol, and hints that this action takes place more readily in the presence of "nascent glycerine" (meaning possibly the hypothetical radicle "glyceryl"). Allen ("Commercial Organic Analysis" vol. ii. 293), has evidently formed a similar conception to this last; the statement the glycerol on heating with caustic potash is easily converted into a mixture of acetate and formate occurs in the majority of text-books, and is founded on the observations of Dumas and Stas (*Ann. Chem. Pharm.*, 35, 158), who found that by heating solid caustic potash and glycerol together they could obtain an acid having a mean composition corresponding to that of a mixture of equal molecular proportions of acetic and formic acids, which reduced silver strongly. Redtenbacher (*Ann. Chem. Pharm.* 57, 174), obtained acrylic acid, and Herter found among other products (fermentation) lactic acid (*Ber.* 11, 1167); with regard to these last, Erlenmeyer's observation (*Ann. Chem. Pharm.* 191, 376), that acrylic acid gives on fusion with caustic potash a mixture of acetate and formate, and Hoppe's

(*Z. f. Physiol. Chem.* 3, 352), that lactic acid is broken up into a mixture of fatty acids, chiefly of the acetic series, shed considerable light on the reaction which takes place, and show that the change is by no means so simple as the equations given assume it to be, but that a series of reactions occur involving first the formation of hydroxy-acids, and their subsequent decomposition, formic, acetic, and other acids being the ultimate products. None of the reactions mentioned above take place at a temperature below  $250^{\circ}\text{C}$ ., a fact which negatives the supposition that under the conditions of the Reichert-Wollny process any volatile acid is formed from the glycerol, and that it is not formed from the "nascent glycerine" is shown by the fact that on saponification of olive, earthenut, or other oils, no appreciable quantity of volatile acid can be obtained, even although the oil be heated with caustic alkali for several hours on the water bath, v. Raumer (*Arch. Hyg.*, 1888, 407), however, states that on heating butter for a considerable length of time with caustic potash, he finds an increase in the quantity of volatile fatty acids estimated by Reichert's process, and this is the only fact that tends in any way to justify the supposition that volatile acids are formed during the saponification.

I therefore consider that we have no evidence that the fatty acids distilled over in the Reichert-Wollny process contain any other than those natural to butter, and as, as far as I can ascertain, there is no evidence that "Propionic, Acetic or Formic Acids" occur naturally in butter, I should be very glad to know the authority for the statement that they are sometimes present in the distillate.

To turn now to the proposed method. On reading over the paper, I was struck by the seeming fact that the titrations of the insoluble fatty acids after saponification were performed in aqueous solution, and on reference to Dr. Johnstone he very courteously informed me that this was the case; there is no indicator which will give satisfactory results under these conditions, litmus, congo-red, and methyl-orange, showing the whole of the combined alkali, while turmeric paper and phenolphthalein give results varying with the dilution, temperature, point taken as the end reaction and nature of the fatty acids. This is what might have been expected seeing that a neutral soap dissociates in the presence of water, the amount of dissociation varying with the temperature, concentration, amount of other substances in solution, etc. c. f. Wright and Thompson (*J. Soc. Chem. Ind.* iv. 630) and Allen (*Co. Org. An.* vol. ii. 245, 260, 265, etc.). The method on this account is totally unreliable.

If from the amount of alkali consumed in saponification (Keottstorfer's figure), we calculate the glyceryl ( $\text{C}_3\text{H}_5$ )" minus the three atoms of hydrogen already contained in the fatty acids, and add to it the amounts of the soluble and insoluble fatty acids, the total should in butters sum up to nearly 100 per cent. (not quite, owing to the soluble acids not consisting entirely of butyric). The figures given in the paper sum as follows:—

|  | A.           | W.           | Y.           |
|--|--------------|--------------|--------------|
| Insoluble Fatty Acids .. ..                            | 89.95        | 90.01        | 89.83        |
| Soluble (as butyric) .. ..                             | 7.35         | 6.26         | 7.67         |
| Glyceryl—3 atoms Hydrogen $\text{C}_3\text{H}_2$ .. .. | 5.18         | 5.09         | 5.09         |
|  | <hr/> 102.48 | <hr/> 101.36 | <hr/> 102.69 |

These are impossible results; that the fault lies chiefly in the estimation of the

soluble fatty acids is shown by the numbers obtained by substituting the amount of soluble acid by the Reichert-Wollny process multiplied by  $\frac{100}{90}$  (which gives a very fair approximation to the total amount of soluble fatty acids contained in the butter; this figure is based on the assumption that 90 per cent. of the soluble fatty acids are distilled over in the Reichert-Wollny process, a number which has been shown to be substantially correct by many observers) *c. f.* Faber (*Anal.* xiv. 98) for the soluble fatty acids; thus:

|  | A.    | W.     | Y.     |
|--|-------|--------|--------|
| Insoluble Fatty Acids .. .. .            | 89.95 | 90.01  | 89.83  |
| R.-W. $\times \frac{100}{90}$ .. .. .    | 4.86  | 4.93   | 5.20   |
| Glyceryl—3 atoms Hydrogen $C_3H_7$ .. .. | 5.18  | 5.09   | 5.19   |
|  | 99.99 | 100.03 | 100.22 |

These figures give a much more satisfactory approach to the correct total, and show that the difference between the soluble fatty acids estimated by the Reichert-Wollny method, and those by the method described in the paper are chiefly due to the errors of the latter; should this method be used by Public Analysts upon samples taken under the "Sale of Food and Drugs Act," a grievous wrong may be done to the vendor.

The three butters, of which the analyses are given, if genuine, come evidently under the head of abnormal butters. The figures for insoluble fatty acids, viz., 89.95, 90.01, and 89.83 respectively, being extremely high, especially with Reichert-Wollny figures of 24.8, 25.2, and 26.6 c.c. (calculated from soluble fatty acids given as by Reichert-Wollny process), a fact which points still more to abnormality. If they are genuine, and can be properly authenticated, they should be placed on record as cases of abnormal butter; it would be most interesting and unusual for three such samples to be in the hands of one analyst at the same time.

In his criticisms of the Reichert process, Dr. Johnstone seems to lose sight of the facts that the estimation of the total volatile acids in butter is as arbitrary and as partial a figure, as far as the analysis of the butter is concerned, as the numbers obtained by Reichert's process, and that Reichert's process is not a method for estimating the volatile fatty acids in butter. I maintain that the Reichert method as modified by Wollny and others is the best and most useful method of butter analysis, on account of its speed and accuracy, it being the method by which two analysts working on the same sample will obtain the most concordant results; and I contend that the information as to the nature of a butter given by this process is at least as accurate and reliable as that given by the estimation of the total soluble acids even could these be estimated with absolute accuracy. As to the statement that Reichert's process does not give any insight into the composition of the volatile acids (which, by the way, it does not pretend to do), I should like to know what method of butter analysis does so? A method which gives better information than the crude results yielded by Duclaux's fractional distillation process, or the fractional liberation of the acids from their salts would be, I am sure, welcomed by analysts.

## ON THE ESTIMATION OF STARCH.

BY PROF. DR. ALEX. VON ASBÓTH.

*(Concluded from page 138.)*

## TEST-ANALYSES.

No. 1.—*Wheat-flour extracted with ether.*

## A. Baryta process.

a. 1.5345 grm.; 10 c.c. baryta require 29.75 c.c. acid; 50 c.c. filtrate require 23.61 c.c. = 64.82 per cent of starch.

b. 1.537 grm.; 10 c.c. baryta require 29.52 c.c. acid; 50 c.c. filtrate require 23.42 c.c. = 64.29 per cent. of starch.

c. 1.537 grm.; 10 c.c. baryta require 29.52 c.c. acid; 50 c.c. filtrate require 23.42 c.c. = 64.29 per cent of starch.

Average percentage of starch, 64.46.

## B. Lintner's process.

a. 3.032 grm.; 25 c.c. solution reduce .1995 grm. of copper = 61.99 per cent. of starch. Residue gave blue with iodine.

b. 3.0335 grm.; 25 c.c. solution, reduce .200 grm. of copper = 62.08 per cent. of starch. Residue colours blue with iodine, and reduces Fehling after treatment with diastase.

No. 2.—*Ground wheat.*

The meal contains 1.78 per cent. of fat and 13.29 per cent. of moisture, and the extracted portion contains 11 per cent. of water.

## A. Baryta process.

a. 1.511 grm.; 10 c.c. baryta require 29.52 c.c. acid; 50 c.c. of filtrate require 23.04 c.c. acid = 69.58 per cent of starch = 66.37 per cent. in the original meal.

b. 1.510 grm. 10 c.c. baryta require 29.53 c.c. acid; 50 c.c. filtrate require 23.015 c.c. acid = 69.88 per cent. of starch = 66.65 per cent. in original meal.

c. 2 grm.; 10 c.c. baryta require 29.85 c.c. acid; 50 c.c. filtrate = 21.31 c.c. acid = 70.17 per cent. of starch = 66.97 per cent. in original.

The average amount of starch is therefore 66.65 per cent.

## B. Lintner's process.

a. 3.003 grm.; 25 c.c. solution = .204 grm. of copper = 63.87 per cent. of starch. After treatment with diastase for twelve hours and inversion with 10 c.c. of acid, the residue yielded a further quantity of copper, corresponding with .83 per cent. of starch.

b. 3.028 grm. Heating was continued for five hours at 145° C. Residue, however, still contained starch. 25 c.c. solution = .202 grm. of copper = 62.74 per cent of starch.

From these analyses we can see that it is impossible to properly estimate the starch by Lintner's process, as the residual mass still contains bodies which may be inverted by diastase.

When I compared the two methods in the analysis of pure starches, and when it was then of course unnecessary for me to use the high pressure flask or to filter the liquids, the results by Lintner's process were certainly satisfactory.

## THE ANALYST.

In conclusion, I must draw attention to an article from H. Schreib, who did not succeed in analysing rice by my process, because the rice-starch would not properly gelatinise. The process in its modified form works, however, very well, as will be seen from the following duplicate analysis of a sample of shelled rice :—

|                     |                |
|---------------------|----------------|
| Moisture .. .. .    | 14.05          |
| Fat .. .. .         | .36            |
| Albumenoids .. .. . | 7.18           |
| Ash .. .. .         | .41            |
| Starch .. .. .      | 76.16—75.98    |
| Cellulose .. .. .   | Not determined |

### ON SOURCES OF ERROR IN DETERMINATION OF NITROGEN BY SODA-LIME, AND MEANS FOR AVOIDING THEM.

BY W. O. ATWATER.

(*Concluded from page 96.*)

The chief sources of loss appear to be from incomplete ammonification and from dissociation of the ammonia formed.

8. The first of these two difficulties is a serious one. With protein compounds, the great trouble is evidently the formation of volatile decomposition products which do not readily yield their nitrogen to form ammonia with hydrogen. This is easy to understand when we consider that protein compounds are prone to yield cleavage products such as leucine and its congeners, compounds allied to the alkaloids, amido-compounds, etc.; and that it is very difficult to get all the nitrogen of these latter into the form of ammonia with soda-lime, evidently because of their proneness to form compounds that resist the ammonifying action.

With alkaloids and allied compounds, leucine and other amido-compounds, amines, and azo- and nitro-compounds, complete ammonification is not always effected, even with the utmost care. Concerning peptones our experience does not enable us to speak; but for the protein of ordinary animal and vegetable substances, including casein, proper precautions appear to insure complete ammonification of the nitrogen. The important condition appears to be sufficient contact with heated soda-lime (*i.e.*, with water vapour at high temperature).

This contact is best secured by (a) intimate mixture of substance with soda-lime; (b) close packing, so as to avoid open space inside the tube; (c) providing a reasonably long anterior layer of soda-lime; (d) heating this latter to dull redness before bringing the heat to bear upon the substance, and keeping it hot until the combustion is done. In order to insure the maximum of surface for contact, it is well to have the anterior layer consist of coarse particles of soda-lime containing enough lime to prevent fusing together. It is possible that too long heating may result in expelling the water from the soda-lime, so that there will not be enough in the latter part of the operation to insure complete ammonification.

Though it is desirable to avoid colouration and turbidity of the acid solution, these do not necessarily imply incomplete ammonification, nor does their absence prove perfect combustion. With proper care to insure contact between soda-lime and substance, we have almost never found the solution so coloured as to seriously interfere with titration.

9. Ammonia may be dissociated and nitrogen lost by either too high heating, or by

conducting the operation so slowly as to leave the ammonia exposed for a long time to heat. It seems probable that the presence of water vapour, as of other gases, would tend to prevent dissociation of the ammonia, and that the danger of long heating may be partly due to reduced supply of moisture from the anterior layer of soda-lime after the latter had been heated for some time.

10. A vacant space in the tube (channel as ordinarily recommended) may cause serious loss. This loss is greater the higher the temperature and the longer the time of combustion. It is probably due not only to incomplete ammonification of distillation products through lack of contact with the soda-lime, but also to dissociation of ammonia. With the channel the flow of the gases is slower, and they are exposed to heat longer than when the tube is packed full. Add the possible lack of water vapour when the heating is long-continued and the loss by dissociation is very clearly explained. When the tube is closely packed, the flow of gases reasonably fast, and the operation conducted at a temperature sufficient to heat the tube only to dull redness, there appears to be no considerable loss by dissociation, even with a long anterior layer (20 or 30 cm.) of soda-lime.

Concerning reagents, apparatus and manipulation, a few words will suffice.

1. *Soda-lime*.—The soda-lime made by mixing one part of ordinary caustic soda with two and a half parts of quicklime by the process described, costs very little for materials and labour, and serves the purpose very satisfactorily. In sifting it is conveniently divided into a finer portion to be mixed with the substance, and into coarser particles to be used for the anterior layer. It bears heating without fusing so much as to leave any considerable open space in the tube if closely packed at the outset. Varying proportions of soda-lime, from 1 part to  $2\frac{1}{2}$  parts of lime to each part by weight of soda, have made no difference in the results of the analyses. We have obtained equally good results with the mixture of sodium carbonate and slacked lime as described by Johnson, and see no reason why slacked lime, as recommended by him, should not be generally efficacious as it has proven in the cases cited by him and in those tried by ourselves. Our reason for adhering to the ordinary soda-lime has been the impression that by filling the anterior portion of the tube with coarse particles of the rather difficultly fusible material, more complete contact is insured between nitrogenous distillation products and the heated water vapour from the soda-lime. The old theory that enough soda should be mixed with the lime to make the mixture easily fusible does not stand the test of experience.

In testing the purity of soda-lime by sugar, as is sometimes recommended, there is danger of error both from the presence of nitrogen in the sugar and from formation of acid distillation products.

2. *Tubes and charging*.—For ordinary combustions, tubes of from 35 to 40 cm. in length do very well. The method of charging the tube, upon which we have gradually settled after numerous trials with tubes of different lengths and charged in different ways, is explained in the accompanying tabular statement:

|                                       |     |     |     |     |     |        |
|---------------------------------------|-----|-----|-----|-----|-----|--------|
| Length of tube                        | ... | ... | ... | ... | ... | 40 cm. |
| Asbestos and fine soda-lime           | ... | ... | ... | ... | ... | 4 "    |
| Mixture, fine soda-lime and substance | ... | ... | ... | ... | ... | 16 "   |
| Rinsings, fine soda-lime              | ... | ... | ... | ... | ... | 4 "    |
| Anterior layer, coarse soda-lime      | ... | ... | ... | ... | ... | 12 "   |
| Asbestos, open space, plug            | ... | ... | ... | ... | ... | 4 "    |

With a shorter tube the divisions may be made proportionately shorter. We intend to have at least 40 parts by weight of fine soda-lime for every part of substance in the "mixture." About 0.4 and 0.6 of flesh (water free), or corresponding amounts of other

materials, we find convenient. The importance of fine pulverisation of substance, intimate mixture with soda-lime, filling the tube compactly so as to have no channel, avoiding the shaking by which particles of the substance might be brought to the top of the soda-lime, and heating until no charred material is left, has been dwelt upon. An anterior layer of coarse soda-lime, 12 centimetres long, has proven very satisfactory. The anterior layer should be well heated before the heat is applied to the mixture of soda-lime and substance, and kept hot until the combustion is done.

3. *Heat and time of combustion.*—A "low red" heat ordinarily suffices. Heating to bright redness brings danger of loss of ammonia by dissociation, though in our experience, when the tube is closely packed and the operation not too slow, we have found practically no difficulty in getting all the nitrogen as ammonia even at high heat. But with a channel in the tube the loss by high heating has been considerable.

Ordinarily, three quarters of an hour is ample for the combustion, and an hour the extreme limit, according to the experience in this laboratory. Rapid combustion is less and long heating more dangerous than is frequently taught. With an ordinary Knop and Arendt (four bulb) bulb apparatus containing 10 c.c. of acid solution, of which little over half was required to neutralise the ammonia, the ammonia was completely absorbed even when the combustion lasted only twelve minutes. Serious loss may result from too long heating, especially if there be open space in the tube or the temperature is high.

4. *Determination of the ammonia.*—In the combustion of ordinary protein compounds with the precautions stated above, practically all the nitrogen is converted into ammonia, and its determination by titration is easy. We find it well, however, to use concentrated solutions, and to avoid excess of water in rinsing out the bulbs. The quantity of concentrated acid solution required is small, and the tension in the combustion tube during the heating consequently slight, which is a convenience; while, with the small quantity of solution in titrating, the colour reaction is sharp, and the determination easy and accurate. Freshly prepared cochineal solution is the most satisfactory indicator we have found. Very narrow burettes, in which 10 c.c. occupy from 30 to 40 cm., have decided advantages for convenience and accuracy when concentrated solutions are used.

## CORRESPONDENCE.

[*The Editor is not in any way responsible for opinions expressed by his correspondents.*]

*To the Editor of the ANALYST.*

### "AN EXPERIENCE."

DEAR SIR,—Some time ago you stated your intention of publishing matters of interest in connection with prosecutions under the Food and Drugs Act. If the following agrees with your ideas on the subject, perhaps you will be good enough to find room for it.

In May last a sample of whisky was sent to me for analysis from a local borough, and my analysis showed that it was 41° U.P. This result was arrived at, in the first instance, by the Westphal balance, and then by distillation and determination of the gravity of distillate by a corrected gravity-bottle and fine balance. The two results agreed within half a per cent. On the strength of my certificate a summons was issued against the vendor, whose defence, at the hearing of the case, was that he had had his portion of the sample analysed by another analyst who made it 18° U.P. In consequence, the third portion was sent up to Somerset House. The chemists there made it 22·5 U.P. Naturally, the charge was dismissed, and if I had not been very sure of my work, I should have had every opportunity of feeling very sorry for myself. Being innocent, however, of any transgression, I made up my mind that on this occasion only the wicked should perish, and I at once set to work to discover how the business had been managed. I went through my copying books, and found that a sample of whisky had been sent from the same borough in January last. That it was 42° U.P., and that the vendor had paid £1 12s. 6d. for his share in the transaction, and had not appealed to Somerset House. Here was light! and careful search through a capacious cupboard, wherein are kept all empty packages having anything to do with food and drugs, gave me more light, for here I found the January bottle, bearing a label and number corresponding in every way with the label and number on the



bottle sent in May, and differing entirely from the labels attached to any other sample sent in May. Two of my staff now went down to interview the Inspector, and they requested a sight of the January sample retained by him. With this, of course, he was unable to oblige them, because, as it was proved further on, he had sent it to me, instead of a portion of the May sample. I now wrote to the Principal of the Laboratory at Somerset House, asking for the bottle he had received to be returned. I was met in the kindest manner possible, and had the satisfaction of knowing that the bottle had been sent to the Justices' Clerk, protected by the official seal. A gentleman from my laboratory now waited upon this same Justices' Clerk to request the privilege of a glance at the label. But to our utter astonishment the seal had been broken, the contents thrown away, and the bottle had been returned to the Inspector!!! I ventured to express my disapproval of this act of the Clerk, and to suggest a different line of conduct upon any similar future occasion. I am sorry to say I gave offence, although I put my protest into the most fatherly language I could command. The Inspector, I am bound to say, gave the bottle up frankly on application, and it was then discovered that I had never even seen any portion of the sample sent to Somerset House, but had re-analysed the January sample. A letter was received subsequently from the Inspector admitting this completely. He said, "I find that when my assistant placed the bottle containing sample of whisky taken on May 4th in the closet, the third portion of sample analysed by you in January, and certified to be deficient in proof spirit to the extent of 17.06 per cent., had been accidentally left in the same closet, and, both being marked No. 1, it is evident that the samples were accidentally transposed."

## MORAL.

And so the poor analyst escaped, and his character was not blasted all to pieces; but if he had not looked precious sharp after his own interest, and done his work properly, and kept his sample-bottles tidy, and copied his certificates into a book where he could readily find the same; and if he had not had a decent, honest man to deal with in the person of the Inspector—seeing how largely his show was discounted by the very curious conduct of the Magistrates' Clerk—he would assuredly not have found himself in the satisfactory position of—Yours truly,

PROOF SPIRIT.

*To the Editor of the ANALYST.*

SIR,—I notice in to-day's *Grocers' Gazette* that Dr. Bernays, Analyst to the St. Saviour's Board of Works, has met with a sample of Condensed Milk similar to the first sample mentioned in my paper on Condensed Milk. It had a label saying that a portion of the cream had been abstracted. The milk was found to contain, when condensed, 0.14 per cent of butter fat, "or about one-twentieth the quantity contained in genuine milk." If the quantity of fat found is not somewhat below that actually contained in the milk, which I think probable, and if the milk was condensed to about one-third, which is likely, as it is recommended to dilute the milk with four parts of water (!), then the "portion of cream abstracted" is no less than 98½ per cent.—Yours truly,

HARALD FABER.

July 13th, 1889.

*To the Editor of the ANALYST.*

DEAR SIR,—Will you please insert in the next number of the ANALYST the following errata and omissions from my paper on "Fat Extraction":—

P. 122, line 10. After Soxhlet insert (*Ding. Pol. J.* 232, 461).

" " 19. After (*Z. f. Anal. Chem.*) insert 1887, 677.

" " 6 from bottom, "7, 8, 9, 11, 13 and 15," read "8, 9, and 13," and insert after "methods," 7. The Copper Sulphate method gives less than Adams' (ANALYST, xiv. 88).

11. See ANALYST, x., 46.

15. See ANALYST, iv., 44, and xiv., 89, *Discussion*.

P. 125, line 7, for '06 read '04.

" " 25, for *Vorhengen* read *Vorschungen*.

P. 126, line 15, for  $\left(\frac{\sigma + \phi}{\sigma}\right) - \frac{G}{D} \frac{1}{\sigma}$

read  $T = F \left(\frac{\sigma + \phi}{\sigma}\right) - \frac{G}{D} \frac{1}{\sigma}$

P. 126, line 8 from bottom, after Besana insert (*Ann. Lodi.* 1886, 31).

P. 126, line 18 from bottom, for  $T = 1.17 F - .263 \frac{G}{D}$  read  $T = 1.17 F + .263 \frac{G}{D}$

P. 127, line 9 from bottom, for *einheitllehr* read "*einheitlichen*."

P. 131, line 7 from bottom, for '012 read '01 per cent.

P. 122, line 8 from bottom, for ANALYST xiii. read xii.

P. 125, line 29, for ANALYST viii. read vii.

P. 126, line 6 from bottom, erase from "an examination" to "formulae," on line 3 from bottom. (This statement was based on calculation with an erroneous formula; on re-calculation I find it is incorrect, and therefore withdraw the statement.)—Yours truly,

H. DROOP RICHMOND.

# THE ANALYST.

SEPTEMBER, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The annual country meeting was held in Liverpool on Friday, the 19th July. In the course of the afternoon a visit was paid, on the invitation of Dr. Campbell Brown, to the laboratories of University College, after which the members and friends dined together at the Grand Hotel. In the unavoidable absence of the President (who in a letter expressed great disappointment that a pressing demand on his duties as a medical officer prevented his leaving home), the chair was taken by Mr. Allen, among those present being Dr. Campbell Brown, Mr. Norman Tate, Dr. Voelcker, Mr. Smetham, Mr. Thomson, Mr. Embrey, Mr. E. Davies, Mr. Faber, Mr. Duncan, Mr. Bernard Dyer, Mr. Otto Hehner, and several visitors, including ladies. After dinner, in lieu of formal papers, a discussion took place on various professional topics relating more particularly to the work and position of public analysts. On the following morning a visit was paid to the Albert Dock Warehouses and other parts of the Dock Estate, where various specimens of Liverpool imports and exports were inspected, after which most of the party proceeded by boat to Llandudno, remaining at the last-named place until Monday.

*(Conclusion of the Society's Proceedings)*

## A RAPID COLORIMETRIC METHOD OF DETERMINING NITRATES IN POTABLE WATERS.

BY SAMUEL C. HOOKER.\*

IN devising a process for the estimation of nitrates in the minute quantities in which they occur in natural waters, I have not been ignorant of the fact that there are already several very satisfactory ways in which this can be accurately done. I have, however, aimed at greater rapidity than has heretofore been possible.

Fully fifteen years ago, Graebe and Glaser discovered carbazol, and observed that when dissolved in concentrated sulphuric acid, it gave rise to an intensely green solution on the addition of nitric acid. This reaction, which up to the present time has been used

\* *American Chemical Journal.*

only as a means of identifying carbazol, forms the basis of the process to be described. Its extraordinary delicacy renders it particularly suitable for the purposes of water analysis, and enables a quantity of nitric acid, containing as little as  $\frac{6}{10000}$  of a milligram. of nitrogen, to be accurately determined. The reaction is not, however, peculiar to nitric acid; all oxidising agents behave similarly. Graebe and Glaser enumerate chlorine, bromine, iodine, nitrous and chromic acids as giving rise to the same intensely coloured solution. With the exception of nitrous acid, the substances just mentioned are almost invariably absent from natural waters, and may therefore be dismissed from further consideration. There is, however, one other oxidising agent, namely iron in the ferric condition, which is sometimes found in very appreciable quantities, and it therefore became necessary, in studying the influence of the substances in solution upon the process, to give special attention to iron as well as to nitrous acid.

As the result of a number of careful experiments, the following conclusions were arrived at with regard to the application of the process:

(1) No material error will arise in the presence of nitrites in the quantities in which they usually occur.

(2) Iron (in the ferrous or ferric condition), if present in quantities greater than 0.1 part per 100,000, must be removed.

(3) Chlorides, even when present in very small quantities, must be removed.

(4) Carbonate of lime, sulphates of lime, soda, etc., in the quantities in which they ordinarily occur, were not found to influence the determinations.

(5) The presence of easily destructible organic matter, such as albumen, lowers the result; not materially, however, unless present in large excess.

The estimation, briefly described, is made as follows:—

Two cubic centimeters of the water to be examined is mixed with 4 c.c. concentrated sulphuric acid; the mixture is cooled, and a small quantity of carbazol, dissolved in sulphuric acid, added. If nitric acid is present, the solution will turn green on the addition of the carbazol; and the intensity of the colour, by comparison with that produced by solutions of potassic nitrate of known strength, will, within certain limits, indicate the amount of the acid present.

The great majority of waters can be estimated directly without previous concentration, and only a few will need to be diluted. The limits within which the determinations may be safely made are marked by quantities of nitric acid represented by .03 and .40 part N per 100,000. Water containing either less or more nitric acid than indicated by these figures must be concentrated or diluted.

To test the accuracy of the process, a number of solutions were prepared, at my request, containing different quantities of potassic nitrate. In order that my judgment might not be influenced by a knowledge of the amount of nitric acid present, I was kept in ignorance of the strength of the solutions until after the estimations had been completed.

The following are the results obtained:

*Nitric Acid expressed as N in parts per 100,000.*

| Present. | Found. | Error. |
|----------|--------|--------|
| .127     | .130   | + .003 |
| .078     | .075   | — .003 |
| .200     | .190   | — .010 |
| .302     | .300   | — .002 |
| .290     | .290   | .000   |

Average error      -      -      -      -      -      .0036

*Nitric Acid present in the 2 c.c. of Water operated upon, expressed in Decimals of a Gram.*

| Present.      | Found.    | Error.     |
|---------------|-----------|------------|
| ·00001143     | ·00001170 | ·00000027  |
| ·00000720     | ·00000675 | ·00000027  |
| ·00001800     | ·00001710 | ·00000090  |
| ·00002718     | ·00002700 | ·00000018  |
| ·00002610     | ·00002610 | ·00000000  |
| Average error |           | ·000000324 |

The above results are not selected, but include all the determinations that have been made with solutions of unknown strength, with the object of testing the delicacy of the process. It is to be borne in mind that potassic nitrate *only* was present. Considering the extremely minute quantities operated upon, the accuracy of the above results is very noteworthy.

The following reagents are required :

- (1) Concentrated sulphuric acid.
- (2) An acetic acid solution of carbazol.
- (3) A sulphuric acid solution of carbazol.
- (4) Standard solutions of potassic nitrate.
- (5) A solution of aluminic sulphate.
- (6) A solution of sulphate of silver.

(1) The sulphuric acid, used for all purposes in the process, should be almost entirely free from oxides of nitrogen. It may be readily tested by dissolving in it a small quantity of carbazol. If the solution be at first golden yellow or brown, the acid is sufficiently pure ; if it be green or greenish, another and better sample must be taken. It is essential also that the specific gravity of the acid be *fully* 1·84, and it is well to ascertain that this is really the case, as I have found several samples, obtained from sources which are generally thought reliable, to fall considerably below these figures. The acid was in fact worthless for the purpose required. As the success of the process depends upon the proper strength of the acid, I cannot lay too much stress upon this point.

(2) The carbazol used was obtained from Kahlbaum, of Berlin. The acetic acid solution is prepared by dissolving 0·6 gram. in about 90 c.c. of 99-100 per cent. acetic acid, by the aid of gentle heat. It is allowed to cool, and is then made up to 100 c.c. by the further addition of acetic acid. The exact strength of this solution is of no material importance to the success of the process, and the above proportions have been selected principally because they are convenient. The solution will probably remain unchanged almost indefinitely ; but I cannot speak positively in this respect, as my actual experience extends only over a period of several months. The use of this solution merely facilitates the preparation of that next described, which will not keep, and has consequently to be freshly prepared for each series of determinations.

(3) The sulphuric acid solution of carbazol is easily made in a few seconds, but it is advisable to allow it to stand from one and one-half to two hours before using. It is prepared by rapidly adding 15 c.c. of sulphuric acid to 1 c.c. of the above described acetic acid solution. This quantity usually suffices in my hands for from two to three nitrate estimations. When freshly prepared it is golden yellow or brown ; it changes gradually, however, and in the course of one and one-half or two hours it becomes olive-green. I am not able to say positively to what this change is due, but it seems probable that traces of oxidising agents occur in the sulphuric and acetic acids, and that these, although not present in sufficient quantity to act immediately, gradually bring about the reaction described. The greenish colour does not interfere with the process, as might

at first be supposed ; on the contrary, I have observed that the solution is not sensitive to small quantities of nitric acid until it has undergone the change to olive-green, and it is for this reason that I have advised that it should be prepared about two hours before required for use. This solution may be thoroughly depended on for six hours after preparation. The intensities of colour produced by the more concentrated solutions of nitrates after this time, gradually approach to each other and become ultimately the same.

(4) The standard solutions of potassic nitrate are very readily prepared. The solutions which are to be compared directly with the waters examined, may be prepared as required, but if many determinations are to be made with a variety of waters, it will be found best to prepare a complete series, differing from each other by .02 part nitrogen in 100,000. This series may include solutions containing quantities of nitrogen in 100,000 parts, represented by all the odd numbers from .03 up to .39. It will be found convenient to prepare them in quantities of 100 c.c. at a time, from a stock solution of potassic nitrate (b) which contains .00001 gram. nitrogen, or .000045 nitric acid in 1 c.c. Each cubic centimetre of this solution, when diluted to 100 c.c., represents .01 nitrogen in 100,000, and consequently if it is desired to make a solution containing .35 part nitrogen in 100,000 35 c.c. are taken and made up to 100 c.c., and so on. The solution of potassic nitrate (b) is best prepared from a stronger one (a) containing .0001 gram. nitrogen to the cubic centimetre, or .7214 gram. potassium nitrate to the litre: 100 c.c. of (a) made up to one litre gives the solution (b). It is obvious that the series of solutions above described could be made directly from (a), but by first making (b), greater accuracy is secured.

(5) For purposes which will be presently described, a solution of aluminic sulphate is required, containing five grams. to the litre. The salt used must be free from chlorine and iron ; and the solution should give no reaction when tested, as in the case of a water with carbazol.

(6) The solution of sulphate of silver is required for the removal of chlorine from the water to be examined. It is prepared by dissolving 4.3943 grams. of the salt in pure distilled water and making up to one litre. The sulphate is preferably obtained by dissolving metallic silver in pure sulphuric acid. The solution should be tested with carbazol in the same way as will be presently described for water ; if perfectly pure, no reaction will be obtained. As sulphate of silver is often prepared by precipitation from the nitrate, it is very apt to contain nitric acid, and consequently, if the source of the salt be not known, this test should on no account be omitted.

Having described the preparation of the reagents, the method of making the determinations may now be considered more in detail. Assuming the water to be free from all substances capable of affecting the accuracy of the results, the process is carried out as follows: Two cubic centimetres of the water is carefully delivered by means of a 2 c.c. pipette into the bottom of a test-tube ; 4 c.c. of sulphuric acid is added, and the solution thoroughly mixed by the help of a glass rod. The test-tube is then immersed in cold water, and when well cooled, 1 c.c. of the sulphuric acid solution of carbazol is added, and the whole again mixed as before. The intensity of the colour is now observed, and a little experience enables a fairly good opinion to be formed of the quantity of nitric acid present. Suppose that the water is roughly estimated to contain about .15 part nitrogen per 100,000, in such a case, solutions of potassic nitrate containing .11, .15, .19 part nitrogen are selected from the series. Two cubic centimetres are taken from each, and treated side by side with a fresh quantity of the water, precisely as described for the preliminary experiment ; the various operations being performed as nearly simultaneously as possible with each of the samples, and under precisely similar conditions. Two or three minutes after the carbazol has been added, the intensity of the colour of each is observed. If

that given by the water is matched by any of the standard solutions, the estimation is at an end. Similarly, if it falls between two of these, the mean may be taken as representing the nitrogen present in cases in which great accuracy is not required. If this be done, the maximum error will be .02 nitrogen, or .09 part nitric acid per 100,000. If greater exactness be required, or it be found that the colour given by the water is either darker or lighter than that given by all the standard solutions, a new trial must be made. In such a case the water must be again tested simultaneously with the solutions with which it is to be compared. This is rendered principally necessary for the reason that the shade of the solutions to which the carbazol has been added is apt to change on standing. Hence it is desirable that the water, and the standard potassic nitrate with which it is to be compared, should have the carbazol added at as nearly the same time as possible. When finally the colour falls between that given by any two consecutive members of the standard potassic nitrate series, the estimation may be considered at an end, and the mean of these solutions taken as representing the nitrogen present. The maximum error in this case will be only .01 nitrogen per 100,000 parts, and the mean error slightly more than .005. This degree of accuracy is believed by the author to be quite sufficient for, if indeed it does not exceed the needs of, all ordinary cases of water analysis for sanitary purposes, for which the process was specially devised. If occasionally, however, greater accuracy is desirable, the determinations recorded in the early portion of this paper show that the average error can be reduced to .0036 part nitrogen per 100,000. In this case the standard solutions employed must differ from each other by .01 part nitrogen only. The additional accuracy gained, however, will scarcely repay for the extra time, care and labour required, and even in this case, as will be seen by a reference to the above determinations, the error may amount to .01 part nitrogen per 100,000.

In the course of a great many experiments I have observed, even when the utmost care has been taken, that two solutions, nominally containing the same amount of nitric acid, occasionally give a very slight though distinctly perceptible difference in shade when tested side by side. Whatever may be their cause, such differences are extremely slight, and if proper care be taken, do not materially affect the value of the process.

I cannot too strongly insist upon the necessity of scrupulous cleanliness at all stages of the analysis. The quantity of water operated upon is so small, that if the greatest care be not exercised throughout, sources of considerable error may be readily introduced. The test-tubes used in the process may be conveniently  $5 \times \frac{5}{8}$  inches in size. They should, of course, be as nearly the same in diameter as possible. It is scarcely necessary to add that they should always be dried when used, and rinsed out carefully with distilled water when put aside.

In comparing the colour given by a water with that produced by standard potassic nitrate, it is necessary only to examine the solution *through* the tubes; differences in shade which can only be detected by looking through the length of the columns of liquid, may be disregarded. It is well to use the same 2 c.c. pipette for measuring both the water and the standard potassic nitrate; the effect of any error in graduation is thus neutralised.

I have made experiments to ascertain whether the intensity of colour produced is strictly proportional to the amount of nitric acid present, with a view to render the use of a colorimeter possible, and thus to avoid the time and trouble necessary to match the colours given by the waters. The result of these experiments, which were made with a Duboscq instrument, shows conclusively that the changes already referred to in both tint and intensity after the addition of the carbazol, occur more rapidly with the light than with the dark solutions, and hence they are not strictly comparable.

*Influence of Nitrites.*

It has been already pointed out that nitrous acid behaves similarly to nitric acid in its action on a sulphuric acid solution of carbazol. In order to estimate to what extent its influence would be felt when present in the water to be examined for nitrates, several solutions of silver nitrite were carefully prepared and estimated precisely as if they contained a nitrate.

The results obtained are given in the following table :

*Results expressed as N in 100,000 Parts.*

| Present as<br>AgNO <sub>2</sub> . | Found. | Error. | Corrected by deducting<br>one-fifth from amount found. |
|-----------------------------------|--------|--------|--|
| ·10                               | ·12    | ·02    | ·096   |
| ·20                               | ·25    | ·05    | ·200   |
| ·30                               | ·37    | ·07    | ·296   |

It will be observed that the error may be very nearly corrected by deducting one-fifth from the amount found. In the presence of nitrates, this correction, of course, will only be possible in cases in which the quantity of the nitrous acid present has been previously ascertained. A correction, however, would be rarely necessary.

*Influence of Iron.*

Although a solution of ferrous sulphate gives no reaction with carbazol, nitrates are apt to be overestimated in the presence of iron in the ferrous condition. Ferric salts, however, acting like other oxidising agents, are themselves able to give the characteristic green colour with carbazol. I have made a number of experiments with solutions of potassic nitrate in the presence of both Fe<sup>II</sup> and Fe<sup>III</sup> in varying amounts, and have ascertained that if iron be not present in quantities greater than 0·1 part per 100,000, the error will not exceed ·01 part in 100,000. The condition of a water with regard to iron may be ascertained sufficiently accurately in a few seconds by the help of ammoniac sulphide. As this is a test which should always be made in the examination of water for sanitary purposes no extra trouble is involved. In a case in which iron is present in large quantities, it can be easily eliminated by rendering the water slightly alkaline, evaporating to dryness, and redissolving the soluble residue in the same volume of pure distilled water as was taken of the water under examination.

*Influence of Chlorides.*

Chlorides form by far the most serious source of error in this process, by intensifying the action of the nitric acid. If, however, nitrates be absent, chlorides give no reaction with carbazol. Were it not for the fact that the chlorine can be perfectly removed in the space of a very few minutes, the general usefulness of the method would be much restricted. In order to remove the chlorine I use the standard sulphate of silver already referred to, 1 c.c. of which, when consumed by 100 c.c. of water, is equivalent to one part of chlorine in 100,000 parts of water. Having first determined the chlorine present, by means of a standard nitrate of silver solution of equivalent strength, the exact quantity of sulphate of silver required is known. I proceed as follows: A flask, graduated at the neck at 100 c.c. and 110 c.c., is filled up to the 100 c.c. mark with the water to be examined. The necessary quantity of sulphate of silver is next added, and then 2 c.c. of the solution of aluminic sulphate previously described; finally, the contents of the flask are brought up to the 110 c.c. mark by the addition of pure distilled water. The whole is shaken up and filtered; the first portion of the filtrate, which will contain any foreign sub-

stances derived from the filter paper, is then thrown away. The aluminic sulphate, by reacting with the carbonates usually present in the water, and thus giving rise to the precipitation of alumina, facilitates the removal of the precipitated chloride of silver, which otherwise, under the conditions given above, is extremely difficult to separate, and may even still pass through the paper after refiltering many times. When the filtrate is perfectly bright, a portion is tested to make sure that all the chlorine is removed; the estimation is then made precisely as already described, the amount found being increased by one-tenth to compensate for the dilution of the 100 c.c. of the water taken to 110 c.c.

It is obvious that such a flask as I have described cannot be used in cases in which the chlorine exceeds eight parts per 100,000, unless the sulphate of silver solution be of greater strength than that which I have recommended. Similar methods will, however, readily suggest themselves.

In a preliminary paper\* published on this process, I mentioned that probably diphenylamine, and other compounds giving similar colour reactions in the presence of concentrated sulphuric acid, might be used instead of carbazol for the *quantitative* estimation of nitrates in water. Shortly after this paper appeared, L. Spiegel† called attention to a process worked up by him, in which diphenylamine was actually used for this purpose. This is briefly described in the *Zeitschrift für Hygiene*, 1887, 2, 189, and was quite unknown to me. Although differing in detail from that which I have devised, the principle is the same, diphenylamine taking the place of carbazol. Spiegel does not mention any experiments made to ascertain the influence of chlorides, but it is probable that this will be found as considerable as I have found it in the case of carbazol.

### REICHERT'S BUTTER TEST.

By DR. BENNETT F. DAVENPORT.‡

THE following minor differences are to be noted between a true butter and a straight oleo, when examined after the Reichert's method.

In the first place, if tasted, the oleo will be found to be deficient in the fulness of flavour of a true butter, while sweet; and it will never acquire the strong flavour and odour of a butter which has turned rancid.

Then when the sample is melted, to allow the curds, water and salt to settle out to the bottom, it will be noticed that the deposit of curds in an oleo will not be more than about one-quarter as much as in a butter. Again, with oleo the saponification is not quite as rapidly completed, and the soap formed is not as rapidly dissolved in the water afterwards added. And when soda is the alkali used, the oleo soap forms a markedly more viscid solution with the water.

Again, in the case of an oleo, a ring of solid deposit forms in the inner tube of the condenser during the distillation, which never occurs at all with a pure butter.

These differences occurring one after another, will enable the analyst to form a fairly reliable opinion as to whether the sample is oleo or butter long before the completion of the distillation.

\* Ber. d. chem. Gessell. 21, 3302; Journal of the Franklin Institute 127, 61.

† Ber. d. chem. Gessell. 21, 3568.

‡ *The Journal of Analytical Chemistry*, Vol. III., Part 2.



THE ESTIMATION OF THE TOTAL ORGANIC NITROGEN IN WATER  
BY THE KJELDAHL PROCESS.

BY HENRY LEFFMANN AND WILLIAM BEAM. \*

CHEMISTS will note with much satisfaction, through the recent communication of Messrs. Drown and Martin, the successful application of the Kjeldahl method to the determination of the total organic nitrogen existing in waters. The so-called albumenoid ammonia process has never been more than a relative determination, and the estimation by the usual combustion method does not seem to be susceptible of general employment in this field. For the benefit of those unfamiliar with the article in question, we present the following abstract :

500 cc. of the water are poured into a round-bottomed flask of about 900 cc. capacity, and boiled until 200 cc. have been distilled off. The free ammonia which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask, after cooling, is added 10 cc. pure concentrated sulphuric acid. After shaking, the flask is placed in an inclined position on wire gauze, and boiled cautiously in a good drawing hood until the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame and a little powdered potassium permanganate added until, on shaking, the liquid acquires a green colour. If the colour is purple instead of green, it shows that the water has not been all driven off. After cooling, 200 cc. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 cc. of sodium hydroxide (200 grams. per liter). The flask is connected with a condenser, shaken to mix the contents, and distilled. The 50 cc. are condensed in very dilute hydrochloric acid free from ammonia. The total distillate is made up to 250 cc., mixed, and 50 cc. taken and Nesslerised. A correction for the nitrogen in the chemicals used is made by means of a blank experiment. From the experiments made, Drown and Martin conclude that the nitrates and nitrites do not interfere with the accurate determination of the organic nitrogen, the error which might otherwise be caused disappearing under the conditions of great dilution which exist in natural waters.

Numerous observations have established the fact that the organic matter of water is susceptible of decomposition or volatilisation by simple boiling, often in such a manner that a notable proportion of the nitrogen is lost. It appeared, therefore, in experimenting on this process, that it would be advantageous to add the acid at once, and thus obtain the nitrogen existing as organic matter, and also in ammonium compounds, estimating that existing in the latter in a separate sample by direct Nesslerising, without distillation ; the calcium and magnesium which would otherwise interfere with the color reaction being removed by the addition of sodium carbonate and hydroxide, according to the suggestion of Morgan. The same principle can be extended to the determination of the ammonium formed by the sulphuric acid. Instead of distilling the liquid after rendering it alkaline, a little sodium carbonate may be added, allowed to stand, filtered, and the filter Nesslerised. In this way the troublesome distillation is avoided. The procedure is as follows :

*Reagents required.*—Concentrated sulphuric acid, as free as possible from nitrogen ; that which we used was of the same make (Baker and Adamson) recommended by Drown and Martin, and contained a similar proportion of nitrogen (.05 mgm. in 10 cc.).

*Sodium hydroxide free from ammonium.*—100 grams. of caustic soda are dissolved in about a liter of water, boiled down to about half its bulk in an open vessel, then diluted to one liter with water free from ammonium.

\* *American Chemical Journal.*

*Sodium carbonate free from ammonium.*—200 grams, pure sodium carbonate are dissolved in a liter of water, and the solution boiled briskly until several hundred cc. have been evaporated.

*Determination of nitrogen existing as ammonium.*—200 cc. of the water are placed in a stoppered bottle, 2 cc. each of the solutions of sodium carbonate and sodium hydroxide added, the stopper inserted, the solutions mixed, and allowed to stand for an hour or two. A filter is prepared by inserting a rather large plug of cotton in a funnel. This should be washed several times with the ammonium-free water. The clear portion of the sample is drawn off with a pipette and run through the filter, the first portions being rejected, since it is diluted by the water retained in the cotton. The filtration is rapid, and when 100 cc. of the liquid has passed through it is Nesslerised. If the ammonium present is very small in quantity, a rather long and narrow tube should be used for observing the colour.

The following are a few of the results obtained with natural waters, and a comparison with the results by the distillation method.

## PARTS PER MILLION.

*Modified Process.*

|  | Nitrogen.        |          |        |
|--|------------------|----------|--------|
|  | In $\text{NH}_4$ | Organic. | Total. |
| Water, already impure, to which decomposing urine was added ... .. | 0.97             | 2.34     | 3.31   |
| Pump-well in densely-populated district ... ..                     | 0.24             | 0.56     | 0.80   |
| Cellar water—impure ... ..   | 0.17             | 0.56     | 0.73   |

*Drown and Martin's Process.*

|  | Nitrogen.        |          |        |                  |
|--|------------------|----------|--------|------------------|
|  | In Free Ammonia. | Organic. | Total. | Lost by Boiling. |
| Water, already impure, to which decomposing urine was added ... .. | 1.25             | 1.82     | 3.07   | 0.31             |
| Pump-well in densely-populated district ... ..                     | 0.33             | 0.38     | 0.71   | 0.09             |
| Cellar water—impure ... ..   | 0.23             | 0.41     | 0.64   | 0.09             |

In uncontaminated waters much less difference, and sometimes none, was noticed between the results by the original and the modified process.

The figures show conclusively, we think, even if there were no other observations on the point, that it is not safe to estimate the ammonium in the water by distillation, nor to boil the water previous to the estimation of the organic nitrogen.

## A SCHEME FOR SEPARATING AND DETECTING SULPHIDES, CYANIDES, FERROCYANIDES, FERRICYANIDES, CHLORIDES, BROMIDES, AND IODIDES IN THE PRESENCE OF EACH OTHER.

By J. S. C. WELLS AND H. T. VULTE.\*

Boil out  $\text{H}_2\text{S}$ , test fumes with  $\text{PbA}_2$ , paper a black coloration indicates  $\text{H}_2\text{S}$ . Add  $\text{NaHCO}_3$  and distil, carrying distillation to dryness, and pass distillate into  $\text{KOH}$ , test this for  $\text{HCy}$  in usual way, when cyanides are removed, cool, dissolve residue in  $\text{H}_2\text{O}$  and add  $\text{CuSO}_4$  as long as a ppt. is formed, and until the liquid becomes blue or green; filter.

\* *School of Mines Quarterly*, X., 3.

| Ppt.                     | Soln.   |
|--------------------------|---|
| Cu, Fe Cy <sub>2</sub>   | Add conc. solution of (NH <sub>4</sub> ) <sub>2</sub> Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> and boil, pass vapour into starch |
| Cu, Fe, Cy <sub>12</sub> | water. Blue colour indicates III when this is removed add a drop  |
| NOTE—Test                | of conc. H <sub>2</sub> SO <sub>4</sub> some dil. K <sub>2</sub> Mn <sub>2</sub> O <sub>8</sub> and boil as long as Br is given off     |
| for these acids          | or until the colour is discharged, adding more K <sub>2</sub> Mn <sub>2</sub> O <sub>8</sub> if necessary.                              |
| in the original          | Finally test soln. with HNO <sub>3</sub> and AgNO <sub>3</sub> , a white curdy ppt. sol. in   |
| with Ferric and          | NH <sub>4</sub> OH and pptd. by HNO <sub>3</sub> indicates HCl.   |
| Ferrous salts.           |   |

NOTE.—So much of the above scheme as relates to separation of Cl Br and I is due to E. Hart (See *Chem. News*, Dec., 1884).

The use of (NH<sub>4</sub>)<sub>2</sub> Fe<sub>2</sub> (SO<sub>4</sub>)<sub>4</sub> is original.

## ON THE DENSITIES AND REFRACTIVE INDICES OF CERTAIN OILS.

By J. H. LONG.\*

IN the course of a somewhat extended investigation on fats and oils I found it desirable to make full determinations of specific gravity and index of refraction.

For some oils these data are not to be found in the literature, and in most cases where given they are more or less incomplete. In the following pages I present the results obtained with oils of known purity, and will describe first the method of experiment.

### *Specific Gravity.*

This was found by means of a 50 gram. pycnometer with capillary stopper, and was determined at four temperatures obtained by immersion in water in the usual manner. A large volume of water was employed, and its temperature kept constant, as shown by an accurately corrected thermometer. The temperature of the oil in the vessel was known to a tenth of one degree C. The volume and cubic expansion of the pycnometer were determined by special experiments. In the final reductions all weights were calculated to the value *in vacuo*, and the specific gravities referred to water at 4° C. as unity.

### *The Index of Refraction.*

For these determinations I employed the method of minimum deviation, making use of an excellent Meyerstein spectrometer and hollow prism, from which readings to 30'' could be obtained. The

refractive index is given by the formula 
$$N = \frac{\sin \frac{A+d}{2}}{\sin \frac{A}{2}}$$
 in which  $A$  is the refractive angle

of the prism, and  $d$  the observed angle of minimum deviation. Some of the experiments were carried out in a cold room in winter, while others were performed in the summer. To determine the refraction at higher temperatures, the prism, resting on its brass table, was placed on a warm iron plate, and allowed to remain there until a thermometer inserted in the top opening of the prism showed the required elevation. The prism and table were then returned to the instrument, their position was adjusted by means of levelling screws, and the readings commenced. (The arrangement of the apparatus is

\* *American Chemical Journal*.

shown in Wullner's *Lehrbuch der experimental Physik*, II., 129.) By making duplicate experiments, and taking the mean values, results accurate to four decimal places of *N* are obtained. In the following tables the corrected temperature readings are given, the thermometer used being the same as that employed in the determination of density. As source of light I used the sodium flame obtained by fusing a bead of sodium carbonate over a Bunsen burner.

*Olive Oil.*

We find various statements in the books regarding the density of pure olive oil. For a temperature of 15° C. the values vary from .9120 to .9250, or even higher. Many chemists claim that these limits are too wide for pure oils, but it must be remembered that the products are extracted and refined by quite different processes. The hot-pressed oils contain considerable palmitin, solidify, therefore, sooner, and show a higher density. Out of a number of samples examined I can report on four of known purity. One of these samples was pressed in Southern California from native olives; the others were pressed in France. Not one of these samples deposited palmitin above 0° C. Although thick, they remained perfectly clear, which suggests to me that the statements usually found in the books regarding the temperature of solidification of olive oil must have been derived from a study of inferior or warm-pressed oils rich in palmitin. Allen, however, gives the solidifying point as +4 to — 6° C.

The specific gravity (D) and the refractive index (N) of these oils I found as follows:—

No. 1. Pressed in France.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 3.5° | .9240 | 14.5° | 1.4716 |
| 19.5 | .9131 | 20.5  | 1.4693 |
| 36.0 | .9022 | 23.5  | 1.4681 |
| 45.9 | .8955 | 26.6  | 1.4673 |
|      |       | 30.7  | 1.4657 |
|      |       | 35.9  | 1.4637 |
|      |       | 41.1  | 1.4620 |

No. 5. Pressed in California.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 4.5° | .9240 | 16.3° | 1.4712 |
| 18.0 | .9149 | 19.3  | 1.4700 |
| 31.1 | .9062 | 23.4  | 1.4684 |
| 49.7 | .8938 | 25.4  | 1.4677 |
|      |       | 29.3  | 1.4663 |
|      |       | 34.3  | 1.4643 |
|      |       | 39.3  | 1.4622 |

No. 10. Pressed in France.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 2.6° | .9252 | 15.8° | 1.4731 |
| 19.5 | .9132 | 20.3  | 1.4708 |
| 33.5 | .9039 | 23.3  | 1.4694 |
| 49.4 | .8935 | 24.8  | 1.4687 |
|      |       | 26.8  | 1.4679 |
|      |       | 30.8  | 1.4663 |
|      |       | 42.2  | 1.4626 |

## No. 11. Pressed in France.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 4.4° | .9238 | 14.8° | 1.4734 |
| 19.8 | .9128 | 17.3  | 1.4722 |
| 32.5 | .9044 | 19.3  | 1.4714 |
| 50.6 | .8924 | 21.8  | 1.4703 |
|      |       | 24.3  | 1.4693 |
|      |       | 27.8  | 1.4677 |
|      |       | 30.8  | 1.4665 |
|      |       | 34.3  | 1.4651 |

The variation in the specific gravity seems to be the same for all samples, and amounts to about .00066 for each degree. Schaedler (*Technologie der Fette und Oele n. s. w.*) gives almost the same coefficient for pure samples, and .9177 as the specific gravity at 15° C. Allen gives .914 to .917 as the probable variations. Quincke (Ber. Acad. Ber. 1883, 409) gives 1.4690 as the value of the refractive index at 20.5° C.

This is close to the values found for Nos. 1 and 5, but somewhat lower than those found for Nos. 10 and 11.

The temperature variation of N amounts to nearly .0004 for each degree between 20° and 35°.

*Cotton-seed Oil.*

Because of the great practical importance and increasing consumption of this article, I have made numerous tests of samples obtained from different sources. In the last few years great improvements have been made in the processes of refining cotton-seed oil, in consequence of which much of the product now on the market does not correspond to the tests usually given. Cotton-seed oil can be refined (and practically is) until it is as clear and light as water. Such an oil contains few of the colouring or readily oxidisable matters which give the so-called *colour* or *heat* reactions so often employed. The cold test (solidifying point) of such oils is likewise very much altered, and their detection when mixed with other oils made more difficult.

I have obtained the following results by direct experiment:—

No. 7. A crude oil obtained in Chicago from a leading refiner. It deposits a sediment quickly when cooled below 15° C.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 3.0° | .9325 | 27.9° | 1.4694 |
| 16.6 | .9233 | 35.3  | 1.4668 |
| 32.4 | .9126 | 46.2  | 1.4624 |
| 46.5 | .9030 |       |        |

The specific gravity determination at the lowest temperature is probably somewhat inaccurate.

No. 8. A light yellow oil, refined from No. 7. Remains clear at lowest temperature.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 4.5° | .9291 | 19.3° | 1.4744 |
| 18.2 | .9198 | 22.8  | 1.4730 |
| 30.9 | .9112 | 24.8  | 1.4722 |
| 45.4 | .9014 | 28.3  | 1.4708 |
|      |       | 36.3  | 1.4675 |
|      |       | 44.2  | 1.4658 |

No. 9. A sample refined from No. 8. This is white and clear, and bears no resemblance to ordinary cotton-seed oils.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 2.0° | .9312 | 18.3° | 1.4736 |
| 17.9 | .9202 | 22.3  | 1.4720 |
| 34.3 | .9090 | 27.3  | 1.4700 |
| 47.0 | .9006 | 31.3  | 1.4684 |
|      |       | 35.3  | 1.4669 |
|      |       | 40.2  | 1.4650 |

No. 12. A crude oil, very dark, but deposits a comparatively small sediment on cooling to 15° C. and below.

The sample is too dark for accurate determinations of the refractive index.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 4.8° | .9290 | 21.0° | 1.4708 |
| 18.6 | .9199 | 23.0  | 1.4700 |
| 32.5 | .9107 |       |        |
| 49.6 | .8994 |       |        |

No. 6. A sample refined from the above in the laboratory, by partial saponification with a 1 per cent. solution of sodium carbonate, washing, and drying by means of a current of hot air. The product is yellow, but perfectly clear.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 3.8° | .9295 | 13.8° | 1.4755 |
| 19.2 | .9191 | 19.3  | 1.4730 |
| 31.4 | .9108 | 23.3  | 1.4712 |
| 47.4 | .9000 | 26.3  | 1.4703 |
|      |       | 32.3  | 1.4681 |
|      |       | 36.2  | 1.4667 |
|      |       | 39.2  | 1.4660 |

No. 16. A clear yellow sample, refined in New York.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 0.7° | .9322 | 19.3° | 1.4742 |
| 15.6 | .9219 | 22.8  | 1.4728 |
| 30.5 | .9117 | 25.3  | 1.4718 |
| 46.5 | .9013 | 27.8  | 1.4708 |
|      |       | 29.8  | 1.4700 |
|      |       | 33.3  | 1.4686 |
|      |       | 36.8  | 1.4672 |

The figures given above show that the temperature variations of specific gravity and refractive index are not very different from those of olive oil. The decrease in specific gravity at mean temperatures varies in the different samples between .00066 and .00068, while the variations in the refractive index are something less than .0004 for each degree.

The values found for the specific gravity of the crude samples are lower than those usually given, as will appear below.

#### *Sesame Oil.*

Although this oil is made in large quantities in Europe, it is difficult to secure specimens here of guaranteed purity.

No. 4. A sample received from a Chicago importer.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 3·3° | ·9308 | 17·9° | 1·4744 |
| 16·5 | ·9218 | 20·4  | 1·4733 |
| 32·4 | ·9111 | 24·4  | 1·4718 |
| 48·8 | ·9001 | 29·4  | 1·4698 |
|      |       | 32·4  | 1·4687 |
|      |       | 36·4  | 1·4672 |
|      |       | 39·3  | 1·4661 |

No. 14. A sample refined from the above by treatment with a 1 per cent. solution of potassium hydrate.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 1·5° | ·9326 | 14·3° | 1·4771 |
| 18·5 | ·9209 | 18·3  | 1·4755 |
| 33·2 | ·9110 | 22·8  | 1·4736 |
| 47·4 | ·9016 | 24·8  | 1·4728 |
|      |       | 26·8  | 1·4720 |
|      |       | 30·3  | 1·4705 |
|      |       | 34·3  | 1·4691 |
|      |       | 39·2  | 1·4673 |

No. 18. A sample received from a New York importer.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 5·5° | ·9282 | 14·3° | 1·4759 |
| 18·4 | ·9192 | 19·3  | 1·4739 |
| 34·6 | ·9081 | 20·3  | 1·4736 |
| 46·6 | ·8998 | 23·3  | 1·4724 |
|      |       | 26·8  | 1·4710 |
|      |       | 30·3  | 1·4694 |
|      |       | 34·3  | 1·4678 |
|      |       | 38·0  | 1·4664 |

The temperature changes are nearly identical with those given for olive and cotton-seed oil, varying for the density between ·00067 and ·00069 for each degree.

*(To be continued.)*

## REGULATIONS OF THE GERMAN GOVERNMENT FOR THE TESTING OF THE MATERIAL USED IN THE DENATURATION OF ALCOHOL.

### 1. WOOD SPIRIT.

WOOD SPIRIT must be colourless or slightly yellowish. On distilling 100 measures under a normal pressure of 760 mm. of mercury, at least 90 measures must come over at a temperature of 75° C. Wood spirit shall be miscible with water without turbidity in all proportions. The amount of acetone shall not exceed 30 per cent. Wood spirit shall decolorise at least 1, but not more than 1·5 per cent. of bromine.

1. Colour.—The colour of the wood spirit shall not be darker than a solution of 2 cc.  $\frac{N}{10}$  iodine solution in a litre of distilled water.

2. Boiling-point.—100 cc. of wood spirit is measured into a metal flask; to the flask a distillation-tube furnished with beads is attached, which is connected by a side tube to a Liebig's condenser. Through the upper opening a standard centigrade thermometer is introduced, with the bulb reaching below the side tube. The flask is gently heated so

that the distillate runs from the condenser in drops; the distillate is received in a graduated cylinder, and shall, when the thermometer stands at  $75^{\circ}\text{C}$ . under the normal pressure (760 mm.), amount to at least 90 cc.

If the barometer does not stand at 760 mm., a degree should be added for each 30 mm. For example, at 770 m. 90 cc. should come over at  $75.3^{\circ}$ ; at 750 mm., at  $74.7^{\circ}$ .

3. Miscibility with water.—20 cc. wood spirit shall give, with 40 cc. water, a clear or very slightly turbid mixture.

4. Separation from soda solution.—On shaking 20 cc. wood spirit with 50 cc. soda solution of 1.3 sp. gr., at least 5 cc. of wood spirit, shall separate in half an hour.

5. Amount of acetone.—1 cc. of a mixture of 10 cc. wood spirit with 90 cc. of water are shaken in a cylinder with 10 cc. of a twice-normal soda solution (80 grs. NaHO in a litre). Next 5 cc. of a twice-normal iodine solution (254 grs. I in a litre) are added with continued shaking. The separated iodoform is taken up by strong agitation with 10 cc. of ether (sp. gr. 0.722). 5 cc. of the ether separating after a short time are measured into a tarred watch-glass, by means of a pipette, and allowed to evaporate spontaneously. After standing two hours over sulphuric acid the watch-glass is weighed. The weight shall not be less than .07 gr.

6. Bromine-absorption.—100 cc. of a solution of potassium, bromide, and bromate (containing 2.447 grs.  $\text{KBrO}_3$  and 8.719 grs.  $\text{KBr}$  dried at  $100^{\circ}\text{C}$  in a litre) are mixed with 20 cc. dilute sulphuric acid (one part acid to three parts water). To this mixture, which is a solution containing .703 grains bromine, wood spirit is dropped in with constant stirring from a burette divided in tenths of a cubic centimetre, till the colour is just discharged. Not more than 30 cc. or less than 20 cc. of wood spirit shall be required.

The bromine-absorption test should be performed by daylight.

## 2. PYRIDINE BASES.

Pyridine bases shall be colourless or very slightly yellowish. The amount of water shall not exceed 10 per cent. On distilling 100 measures of the mixture, under a normal pressure of 760 mm. of mercury, at least 90 measures must come over at a temperature of  $140^{\circ}\text{C}$ . The mixture shall be miscible with water in all proportions, without turbidity, and shall be free from ammonia.

1. Colour.—As for wood spirit.

2. Behaviour towards cadmium chloride.—10 cc. of a solution of 1 cc. pyridine bases in 100 cc. of water are mixed with 5 cc. of a five per cent. aqueous solution of fused cadmium chloride, and strongly shaken; a distinct crystalline precipitate must occur almost immediately. With 5 cc. Nessler reagent. 10 cc. of the same solution of the bases should give a white precipitate.

3. Boiling-point.—As for wood spirit, except that at least 90 cc. must have come over when the thermometer reaches  $140^{\circ}\text{C}$ .

4. Miscibility with water.—As for wood spirit.

5. Amount of water.—On shaking 20 cc. of the bases and 20 cc. of soda solution (1.4 sp. gr.) at least 18.5 cc. of the bases must separate on standing.

6. Titration of the bases.—1 cc. of the pyridine bases, dissolved in 10 cc. of water,



are titrated with normal sulphuric acid till a drop of the mixture placed on congo-red paper develops a distinct blue edge which disappears at once.

To prepare the congo-red paper, filter paper is drawn through a solution of 1 gr. congo-red in a litre of water and dried.

[*Note by Abstractor.*—It is in many cases advisable to paint non-bibulous paper on one side with this solution and dry it.]

### 3. TAR OIL.

1. Colour.—The colour of tar oil must be a black-brown.

2. Boiling-point.—When 100 cc. of tar oils are distilled in the manner directed for wood spirit, not more than 5 cc. shall come over under  $90^{\circ}$  C, but at least 50 cc. at  $180^{\circ}$  C.

3. Pyrrol reaction.—2.5 cc. of a one per cent. alcoholic solution of tar oil are diluted with alcohol to 100 cc. On placing a pine-wood chip, wet with concentrated hydrochloric acid in 10 cc. of this solution, containing .025 per cent. tar oil, a distinct red colour shall develop in a few minutes.

4. Behaviour towards mercuric chloride.—5 cc. of a one per cent. alcoholic solution of tar oil shall, on mixing with 5 cc. of a two per cent. alcoholic solution of mercuric chloride, give immediately a voluminous flocculent precipitate; 5 cc. of a .025 per cent. alcoholic solution of tar oil mixed with 5 cc. of the mercuric chloride solution shall still yield immediately a distinct turbidity.

### 4. TURPENTINE OIL.

1. Specific gravity.—The specific gravity shall be between .855 and .865 at  $15^{\circ}$ .

2. Boiling-point.—When 100 cc. are distilled in the manner directed for wood spirit, not more than 5 cc. shall come over under  $150^{\circ}$  C, but at least 90 cc. at  $160^{\circ}$ .

3. Miscibility with water.—20 cc. turpentine oil are strongly shaken with 20 cc. of water, when, after standing, both layers have separated and become clear, the upper one shall amount to at least 19 cc.

### 5. ETHER.

1. Specific gravity.—The specific gravity of ether shall not be more than .730.

2. Miscibility with water.—20 cc. of ether are strongly shaken with 20 cc. of water. After the separation the ether layer shall amount to at least 18 cc.

### 6. SHELLAC SOLUTION.

10 grs. of the solution, on evaporating on the water bath, and drying for half an hour at  $100^{\circ}$ – $105^{\circ}$ , shall give at least 3.3 grs. shellac.

H. D. R.

## REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

VOLUMETRIC ESTIMATION OF ZINC. A. VOIGT. *Zeitschr. f. angew. Chemie*, No. 11, 1889.—The sample, which may be any kind of zinc ore or zinc refuse, is dissolved in hydrochloric acid, oxidised with a little nitric acid, and rinsed into a measure with about 100–150 c.c. of water. According to the amount of iron present, from 5 to 10 grammes of potassium tartrate are added, the liquid made alkaline with ammonia, and then made up to 250 c.c. Standard solution of potassium ferrocyanide is now added, until a drop of the liquid produces a permanent blue with a drop of glacial acetic acid. The reaction is very delicate and readily noticed. The ferrocyanide solution is prepared by

dissolving 46 grammes of the crystals in a litre of water. To standardise this solution, a zinc chloride solution is used, containing 12.461 grammes of zinc oxide per litre. Ten c.c. of this solution are diluted to 150 c.c., mixed with a few drops of ferric-chloride, then with 5 grammes of potassium tartrate, and after being made alkaline, with ammonia, treated as described. If less than 10 c.c. of the ferrocyanide are wanted, this solution must be accordingly diluted, when 1 c.c. will represent .01 gramme of metallic zinc. This process will give results somewhat too high if the ore contains much manganese, but small quantities of lead do not in the least interfere.

L. DE K.

VALUATION OF INDIGO. M. HONIG. *Zeitschr. f. angew. Chemie*, No. 10, 1889.—From .5 to .8 gramme of the finely-powdered sample is mixed with about 2.5 grammes of finely-divided dry pumice-stone. The mixture is brought into a Zulkowsky-Wolfbauer extraction apparatus (a kind of Soxhlet), covered first with a layer of powdered pumice-stone, and then with cotton-wool. The extraction is performed with 50 c.c. of anhydrous aniline or nitro-benzol, and is generally completed in an hour. If thought necessary, the mass may be removed from the apparatus, washed with alcohol, dried, powdered, and extracted a second time. The solution is distilled off to recover the aniline, but it is impossible to carry the distillation to dryness on account of bumping. The contents of retort are therefore emptied into a little graduated measure, when the volume must be carefully noted. About five times the volume of absolute alcohol is now added, the precipitated indigotin collected on a weighed filter, washed with alcohol until washings are almost colourless, dried at 110° C., and weighed. To the weight obtained must be added .013 gramme for every 10 c.c. of aniline left, or, .021 gramme if nitro-benzol has been used. On the whole, the author prefers using aniline. The indigotin must, of course, be tested for sandy matter.

L. DE K.

TEST FOR LINOLEIC ACID IN COMMERCIAL OLEIN.—K. HAZURA. *Zeitschr. f. angew. Chemie*, No. 10, 1899.—Fifty grammes of the sample are saponified with alcoholic potash, and after driving off the spirit, dissolved in 1 litre of water. The solution, which must be strongly alkaline, is now slowly mixed with a solution of 50 grammes of potassium permanganate in a litre of water. After about an hour, the liquid is filtered off from the precipitated hydrated manganese dioxide, acidified with dilute sulphuric acid and again filtered. The filtrate is neutralised with caustic potash and evaporated down to about 300 c.c., and then once more acidified with sulphuric acid, which will again cause a precipitate. Without filtering, the fluid is now agitated with ether. If the precipitate dissolves completely, it merely consisted of azelaic acid, and the sample may be considered pure; but if insoluble, linoleic acid is most likely present. To make sure, the precipitate is washed and recrystallised a few times from its alcoholic solution, animal charcoal being added to decolourise. After drying, the melting point is taken, which should come to at least 160° C. If a sufficient amount of this substance should be at disposal, its acidity equivalent may be taken. This should not exceed 150°. By these tests the presence of linoleic acid in commercial oleic acid may be shown with certainty.

L. DE K.

SUBSTITUTE FOR CALCIUM CHLORIDE TUBE IN ELEMENTARY ANALYSIS. JOS. PREUSSER (*Z. f. Anal. Chem.* 28, 322).—Schmitz has described (*Z. f. Anal. Chem.* 23, 515) an apparatus consisting of a U tube containing phosphoric anhydride in the first limb, and sulphuric acid in the second; the  $P_2O_5$  being soon used up, the author prefers to place

in the first limb a tube containing sulphuric acid, through which the gas bubbles, and to place the phosphoric anhydride in the second. A drawing is given of the tube as made by Gerhardt in Bonn.

H. D. R.

THE QUANTITATIVE ESTIMATION OF THALLIUM AND MERCURY. W. FEIT (*Z. f. Anal. Chem.* 28, 314).—Thallium is generally estimated by precipitation as thallous iodide, but as this salt is not entirely insoluble, the results are not wholly reliable.

Thallic salts react with potassium iodide, forming thallous iodide and free iodine, which the author titrates with arsenious acid solution. The substance is converted into thallic sulphate by the addition of sufficient sulphuric acid, and if necessary the thallous salt oxydised by adding a slight excess of bromine and boiling off the excess; cool, and add an excess of potassium iodide, neutralise the free acid, and add about half as much again of  $\frac{N}{10}$  arsenious acid solution (4.942 grs.  $As_2O_3$  in 1 litre) as is required to combine with the iodine, make up to bulk, filter, and titrate an aliquot portion with  $\frac{N}{50}$  iodine solution. 506.16 grs. I = 407.2 grs. Tl.

The test analyses are—

Calculated for  $Tl_2SO_4$ .

Gravimetric.

Volumetric.

81.12

79.56, 79.47

80.12, 80.14, 80.20, 80.31, 80.31, 80.11

Mercuric oxide is quantitatively reduced by arsenious acid to metallic mercury; the substance to be examined is brought into solution as mercuric salt, precipitated with a slight excess of caustic soda, somewhat more than the necessary amount of  $\frac{N}{10}$  arsenious acid solution added, heated, with constant shaking, to boiling, and left to stand for ten minutes, cooled, and made up to bulk, and an aliquot portion titrated after filtration with  $\frac{N}{50}$  iodine solution with starch as indicator.

Test analyses :—

Calculated for  $HgCl_2$ .

Found.

73.80

74.23, 73.73, 74.13, 74.49, 73.89

Calculated for  $HgO$ .

Found.

92.59

92.79, 92.45

H. D. R.

## LAW NOTES.

### MILK OF SULPHUR AND PRECIPITATED SULPHUR.

At the Dalston Police Court, before Mr Haden Corser, magistrate, on August 8th, Mr. Alfred F. Gray, 93 Grosvenor-road, Highbury, pharmaceutical chemist, was summoned by George Morgan, an inspector in the employ of the Vestry of St. Mary, Islington, "for that he did, on the eighth day of July, 1889, sell, to the prejudice of the purchaser, a sample of a certain drug, to wit, milk of sulphur, which was not of the nature, substance, and quality demanded by the purchaser, the said milk of sulphur containing 6.9 per cent. of calcium sulphate, contrary to the provisions of the Sale of Food and Drugs Act 1875, 38 and 39 Vic. c. 63, and the Sale of Food and Drugs Amendment, 1879, 42 and 43 Vic. c. 30, being the statutes in such case made and provided."

Mr. Collingwood, chief sanitary officer, represented the Islington Vestry, and the defendant conducted his own case.

Mr. Collingwood said this was a summons taken out by the Vestry of St. Mary, Islington, against a chemist, and a very respectable one, for selling a sample of sulphur containing calcium sulphate.

Mr. Haden Corser: What does the defendant say?

Defendant: I plead not guilty.

Mr. Collingwood: He must be prepared to fight the analyst, not me. I may say, however, as a preliminary, that Mr. Gray desired that the analyst might be present, and that has been acceded to.

George Morgan was called and deposed that he was an inspector of nuisances for the parish of St. Mary, Islington. On July 8th he went into the shop of defendant, who is a chemist, and asked for a quarter of a pound of milk of sulphur, for which he paid 3d. He told defendant he was an inspector, and divided the sulphur into three parts, giving defendant one portion, keeping one himself, and the same day forwarding the remainder to the public analyst.

The certificate of the public analyst was here put in. The analyst stated that the sample of milk of sulphur received by him weighed about  $1\frac{1}{2}$  oz., and contained 6·9 per cent. of calcium sulphate, to the prejudice of the purchaser.

Mr. Collingwood : I may tell your worship that this milk of sulphur is a powder.

Mr. Haden Corser : Thank you ; I already knew it. (Laughter.)

Mr. Collingwood : This calcium sulphate our analyst alleges to be an adulterant, and he is present to support his certificate.

Morgan, in cross-examination by Mr. Gray, said he asked for milk of sulphur. He did not ask for precipitated sulphur, because he did not want it.

Defendant : Did I look at this book (produced) to see what to charge you ?—Yes.

Defendant (to the magistrate) : In this printed book it says, "milk of sulphur, 3d.," and "precipitated sulphur, 4d." the quarter-pound. This was distinctly sold as milk of sulphur, and not as precipitate. (To the inspector) : Do you know the difference between the two substances ?—No.

Mr. Collingwood : He would not know. He was merely instructed to buy milk of sulphur. If his worship, under the circumstances, sees a way for you to get out of your difficulty we have no objection. (laughter.)

Dr. Frank Teed, 8 Victoria Chambers, Westminster, put in his certificate of appointment as public analyst for the parish of St. Mary, Islington. He said : I have examined the milk of sulphur bought at defendant's shop, and find it to contain 6·9 per cent. of calcium sulphate. Milk of sulphur and precipitate of sulphur are one and the same thing, or least they ought to be.

Defendant : What authority have you for that.

The Magistrate : One moment. Can you ask for the one or the other ?

Mr. Collingwood : In asking for milk of sulphur the inspector was right, as proved by the fact that he got it.

Dr. Teed : Any extraneous matter in the sulphur is an adulterant. I say the milk of sulphur and the precipitated sulphur are one and the same thing. I take the extract from Watt's "Dictionary of Chemistry."

The Magistrate : I cannot take that. But you know what these substances are ? You say that this milk of sulphur should contain nothing but sulphur. I see there are different prices for the two kinds in the list.

Defendant : I suppose you know, Dr. Teed, that milk of sulphur is in the old Pharmacopœia, if it is not in the new ?

Dr. Teed : It is not in the present one.

Defendant (producing old book) : It is in this, the old Pharmacopœia ; and ever since it was laid down in this book the two articles have been manufactured and sold as distinct articles.

The Magistrate : You say that you sell them in different ways and as distinct articles ?

Defendant : Yes ; there is *lac sulphuris* and precipitated sulphur. (To the analyst) : Are these known as distinct articles ?

Dr. Teed : I should think not.

Defendant : This case has been brought up before, your worship, so far back as 1877, at Knutsford, when Mr. Horatio Lloyd, chairman of the bench of magistrates, decided the matter in the following words :—"We have been considering the matter since we left the court, and—"

The Magistrate : You are not quoting from a law report ?

Defendant : No.

The Magistrate : You may read that, and ask the witness if he agrees with it.

Defendant (reading) : "The case having been fully gone into, the Chairman said, 'We have been considering this matter since we left the court—and I am speaking for all the magistrates who heard the case—we think the absence from the Pharmacopœia of milk of sulphur justified the complainants in taking these proceedings ; but we find that milk of sulphur and precipitated sulphur are supplied to the trade as two distinct things. We cannot doubt upon the evidence that the offence has not been made out.' " I submit, therefore, there is no case. Will your worship allow me to ask the analyst if he will accept the verdict of the Pharmaceutical Society on the matter ?

The Magistrate : No. Give him the opinion, and ask him if he agrees with it.

Defendant (to the analyst) : Do you accept what the old Pharmacopœia lays down in the matter ?

Dr. Teed : The old Pharmacopœia is not allowed to be used now, and the two things are not in the new Pharmacopœia.

Defendant : But it does not follow that the two things are the same.

In reply to the Magistrate, Dr. Teed said : For some years the two things have been known under one name.

By Mr. Collingwood : I quite understand that the milk of sulphur and the precipitated sulphur are one and the same thing. The title has been dropped in the one. Milk of sulphur is the chemical name of precipitate of sulphur.

The Magistrate : The defendant can go into the box and give evidence.

Mr. Gray was therefore sworn, and said : The article I sold is milk of sulphur. I was asked for that, and I supplied the article which answers to the description.

The Magistrate : Did you know the composition of the article you were asked for ?

Defendant : It is a compound containing calcium sulphate. In the process of manufacture it is impossible to remove the whole of the calcium sulphate.

The Magistrate: Is the milk of sulphur manufactured by yourself?

Defendant: No. I purchased it.

The Magistrate: Was the purchase in accordance with the rules of the Pharmacopœia?

Defendant: Yes, under the old one. Lac sulphuris is the old one which I have here. The new Pharmacopœia has only precipitated sulphur. I sell the articles at different prices, and have them supplied the same.

Mr. Collingwood: Is it not a fact that the old Pharmacopœia has been declared illegal?

Defendant: Not to my knowledge.

Mr. Collingwood: I am told that in a recent case affecting sal volatile the old Pharmacopœia was declared to be illegal.

Defendant: I can explain that. Sal volatile in the new Pharmacopœia is ordered to be made in a different manner to the old. That is the standard work which is accepted as an authority.

The Magistrate (to Mr. Collingwood): What I understand you to say is this, that because milk of sulphur is not in the new Pharmacopœia it should not be supplied at all?

Mr. Collingwood: Precipitated sulphur should be given. (To Defendant): I think you said in your evidence that it is impossible to separate the calcium sulphate from the precipitated sulphur, and then you say you sell both articles.

The Magistrate: He says in his judgment they differ.

Defendant: It is precipitated by hydrochloric acid.

Mr. Collingwood: Cannot the sulphate of calcium be washed out?

Defendant: That is not the way in the new Pharmacopœia.

By the Magistrate: I cannot say if it can be all washed out. It might in time all get washed out.

The Magistrate: What is the object of keeping the two sorts?

Defendant: Because people will have what they ask for. And plenty of doctors will give evidence that milk of sulphur is more soluble and more beneficial.

Mr. Collingwood: It is not known in the new Pharmacopœia. That is our case.

The Magistrate: Is the British Pharmacopœia absolutely binding upon chemists?

Mr. Collingwood: I believe it is, sir.

The Magistrate: If this gentleman had been asked for an article which is not in the British Pharmacopœia, but which according to his judgment he supplies, is there anything to prevent him?—No reply.

The Magistrate: If he was asked for milk of sulphur, should he say he had not got it?

Dr. Teed: He should have supplied the precipitated sulphur.

The Magistrate: I should like very much the judgment of a superior court on such a matter as this. This vestry official goes in to purchase an article which he knows he will not get according to his own views. You (addressing Mr. Collingwood) knew defendant sold the two kinds probably. He asks for and gets what defendant calls milk of sulphur, and Dr. Teed says that is not known in the British Pharmacopœia. But the defendant says, and Dr. Teed does not deny, that it is in the old Pharmacopœia, which you say is now obsolete.

Mr. Collingwood: I will not further trespass on the time of the court, but leave the case in your worship's hands.

The Magistrate: And I need not enter into a lengthy judgment in the case. Defendant has been asked for an article known as milk of sulphur, and the purchaser gets what manufacturers and the public know as milk of sulphur—

Mr. Collingwood: I am afraid the public do not know the composition of it.

The Magistrate: I hold that he has not got this article to the prejudice of the public, and shall dismiss the summons. He had the precipitate of sulphur as well if anybody wanted it, and the prices of the two articles were different.

Mr. Collingwood: We have had milk of sulphur over and over again which has not contained calcium sulphate.

Defendant asked for his costs, but the magistrate thought there was no necessity for allowing them.—*Chemist and Druggist.*

## CORRESPONDENCE.

[The Editor is not in any way responsible for opinions expressed by his correspondents.]

To the Editor of the ANALYST.

Note (?) in a recent paper by Dr. Johnstone.

SIR,—I have neither the time or inclination to commence a controversy in the pages of the ANALYST with such a young and inexperienced hand as Mr. Richmond, more than to state that the three samples of butter were, without doubt, genuine, and through your kindness they have already been "recorded" in the ANALYST. I also most emphatically deny ever having informed your self-opinionative contributor, who is strong in the infallibility of his own judgment, that I titrated the insoluble acid in an aqueous solution, and I can assure him that dissociation did not take place in the soap solutions titrated by me.

Crieff,

23rd August, 1889.

Yours faithfully,

WILLIAM JOHNSTONE.

# THE ANALYST.

OCTOBER, 1889.

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## A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF FAT IN MILK, SKIMMED MILK, BUTTER-MILK, AND CREAM.

BY CHARLES L. PARSONS.

THERE have been, within the last few years, so many improvements in breeds of cattle and in the production of milk, butter, and cheese, that no creamery-man, dairyman, or farmer can ignore them and still hold his own against the increasing competition of the day. Breeds of cattle and individual cows must be kept which pay for the food they consume by their milk, or they must be turned into beef. Butter must be made which comes up to the standard in flavour, colour, and grain. Milk must be sold which meets the requirements of the law, where it is to be consumed as such, and where it is to be used in making butter, quality as well as quantity will soon determine the value. But, one may ask, on what basis shall one cow be kept and another rejected, or milk be bought and sold? The question has been many times answered. Quantity was formerly the basis, but now the amount of butter-fat which the milk contains must have equal consideration. The quantity is easily determined by measures or scales, but to determine the fat has been quite another matter.

Every butter-maker, in order to compete with others, must soon know the amount of fat in the original milk, the amount he has obtained in his cream, and the amount lost in the skimmed milk and buttermilk. There has long been an increasing demand for some quick, simple, cheap, and accurate method which is applicable to all four.

Butter-makers have been satisfied with general deductions from analyses at some distant laboratory, but now, from the demonstrated differences of the effect of individuals, breed, food, and temperature upon the churnability of cream, they must be made often, and at home.

Different herds vary greatly in the quality of milk which they produce. This is shown plainly by the results of analyses given in the second annual report of the New York Dairy Commission. The average milk of seventy dairies there reported varied between 3.08 per cent. and 6.60 per cent. of butter-fat. It is manifestly unfair to every creamery and progressive farmer that the same price should be paid for milk containing three per cent. of fat as for milk containing double that quantity.

Many methods have been devised to be used for "testing milk." Feser's lactoscope, the lactobutyrometer, the creamometer, the oil-test churn, Heeren's milk-tester, the methods of Vogel, Soxhlet, and Short, and the lactocrite have all been proposed for general use and have met with varied success. Of these, the methods of Soxhlet and Short, and the lactocrite, are undoubtedly the best. The expense of the lactocrite, and the ether required by the method of Soxhlet, however, shut them out from many creameries and dairies. Short's method requires no great expense, but while it gives good results on whole milk, in the words of its author, it does not give "accurate results with milk containing under .50 per cent. of fat." This, of course, shuts out the analysis of most skimmed milk and some buttermilks. If a butter-maker is to balance accounts, the fat lost in the skimmed milk and buttermilk must be taken into consideration, as well as the fat in the milk and cream.

I have for some time past been experimenting for the purpose of obtaining a simple and cheap method, applicable to all grades of milk and cream, which would give good results in the hands of any dairyman. The following is the method obtained, and no scientific terms have been used where they could possibly be avoided:—

#### THE APPARATUS.

1. (a) Three pipettes. No. 1, to hold 100 cubic centimeters; No. 2, to hold 50 cubic centimeters; No. 3, to hold 25 cubic centimeters, and having the lower stem at least nine inches long. (b) A measuring-cylinder holding, when full, 10 cubic centimeters. (c) A measuring-tube nine inches long and of such an internal diameter that the distance on the scale from zero to five shall be between seven and one-half and eight inches. These tubes are accurately calibrated, and are marked on the outside. The numbers 1, 2, 3, 4, and 5 on the scale represent so many whole cubic centimeters. The distance between 0 and 1, 1 and 2, etc., is divided by twenty lines, the distance between two of these subdivisions representing .05 of a cubic centimeter.

2. One or more long, slender bottles made of transparent glass, eleven inches high and one and one-half inches in diameter, which hold about 250 cubic centimeters. The neck should fit a No. 2 rubber cork.

3. One or more flasks of about 70 cubic centimeters' capacity, with the neck cut off obliquely, and of a size and length to go into the top of the measuring-tube.

4. A drying-oven, eight inches wide, twelve deep, and fourteen high, which has a

thermometer, shelf for holding flasks and measuring-tubes, and a single-burner kerosene stove beneath for heating.

#### SOLUTIONS REQUIRED.

1. Gasoline, practically free from anything in solution. This gasoline is that ordinarily used in gas machines. It is sold in three grades ( $86^{\circ}$ ,  $88^{\circ}$ , and  $90^{\circ}$ ), either of which will do. It begins to boil at about  $80^{\circ}$  F. and generally the last portions boil off at  $140^{\circ}$  F. (The substance used in street lamps generally called gasoline is not such, but naphtha, and will not do.)

2. Caustic soda solution. This is made by dissolving in an iron vessel one pound of commercial caustic soda in two pounds of water.

3. Strong alcohol (95 per cent.), in which one ounce of Castile soap to the gallon has been dissolved. To dissolve easily the soap should be scraped fine.

4. A little strong acetic acid.

#### DIRECTIONS FOR ANALYSIS.

Fill the largest pipette to the mark with the well-mixed milk, and run into one of the bottles. Add to it the measuring-cylinder full of caustic soda solution and half full of alcohol soap solution. Then add pipette No. 2 full to the mark of gasoline. Cork the bottle. Shake hard for a few seconds, and again five or six times, at about equal intervals, in the next half hour. After the last shaking let the bottles stand a few minutes to see if the gasoline will not rise to the top. If it does not, add the measuring-cylinder half full of alcohol solution again, and as soon as bubbles cease to rise, turn the bottles slowly upside-down and back again. This may be repeated until four portions of alcohol have been added, or separation takes place sufficiently to draw out the required quantity of the upper liquid. The bottles should be turned slowly in order not to mix again any of the gasoline solution which has separated. This separation generally takes place after the first addition of the alcohol solution.

As soon as the upper solution is perfectly clear, fill the smallest pipette to the mark with it, taking great care that none of the lower solution enters. From the pipette let the solution run into one of the flasks and evaporate the gasoline. Add two drops of acetic acid to the fat which is left behind. Place the flask in the oven and dry it at  $245^{\circ}$  to  $255^{\circ}$  F. for one hour and a-half. Now turn the fat slowly into one of the measuring-tubes previously placed in the oven. Let the flask drip for ten minutes while the oven is at the same temperature. Remove the last drop by drawing the neck of the flask across the neck of the tube. Cool the measuring-tube until the first appearance of the fat solidifying, hold clasped in the hand a moment, and then read off the number on the scale which corresponds with the upper surface of the fat. From the accompanying table ascertain the per cent. of fat which corresponds to this number.

Several analyses can be carried on at once, all flasks, bottles, and tubes being carefully numbered.

#### SKIMMED MILK AND BUTTERMILK.

Skimmed milk and buttermilk are treated nearly the same as whole milk. The fat from either, if less than 1 per cent., need be dried only three quarters of an hour. If more than 1 per cent. it should be treated as a whole milk. It is easy after analysing one or two milks to judge approximately from the amount of dried fat in the small



flasks whether it is above or below this per cent. If the milk is thought to be below 1 per cent., it should be measured in a tube which is already at least half full of dried fat. The reading on the scale for the fat already in the tube should be taken, and the reading after the addition of the fat from the flask. The difference between the two gives, of course, the reading for the skimmed milk or buttermilk.

#### CREAM.

The sample should be carefully mixed, and free from air bubbles. Fill the largest pipette to the mark and let it run out into some suitable vessel. After blowing out the last drops, fill the same pipette with water and mix this well with the cream already measured. With this mixture fill pipette No. 2 to the mark, run it into one of the bottles, and proceed as for whole milk. The fat from very rich cream should be dried for two hours. It is always best to carry on two analyses of milk or cream, whatever method is used, the one to check the other. Results cannot be expected to agree as closely on cream as on milk, for the amount used is only one-fourth as great; nor is the accuracy, necessary in the one case, required for practical work in the other.

#### DETAILS.

*Sampling.*—The milk or cream should be well mixed and free from air bubbles. Fill the pipette a little above the mark on the neck by suction with the mouth, and quickly place a finger (dry) over the top. Then, by gradually letting in air, allow the milk to run out slowly until it just reaches the mark. All solutions measured with a pipette should be measured in this manner. These measurements should be made accurately, especially the measurement of the gasoline solutions. Always allow the pipettes to drip a moment, and blow out the last drops. In analysing milk in creameries where the milk is tested only at intervals, the samples should be as nearly as possible an average one. To this end, mix the night's and morning's milk.

*Treatment of the Gasoline Solution.*—Do not try to hurry the separation, as too much alcohol soap solution is worse than too little. The separation of whole milk or cream generally takes place within ten minutes. Skimmed milk and buttermilk occasionally require a longer time, but will always separate. Sour buttermilk does not separate as easily as fresh, and sometimes has to stand over night. If in filling pipette No. 3 any of the lower solution enters, the whole must be run back into the bottle and allowed to settle again. This need never occur if care is taken to draw up the solution slowly and not by jerks. Before using the small flasks for the first time, each one should have a little pure fat put in and melted. This should be allowed to drip out under the same conditions as in actual analysis. (Butter which has been melted and the salt and curd allowed to settle out, or the fat obtained in analysis, is best for this purpose.) A film of fat is thus left behind, which compensates for the fat left behind in analysis. This film is always approximately the same, as in evaporating the gasoline it is each time washed down by the gasoline condensing on the sides of the flask, and is again left when the fat is turned into the measuring-tube.

*Evaporating Gasoline.*—Gasoline takes fire very easily, and should not be evaporated within several feet of a flame, unless protected. It boils much below the boiling point of water. The best way for general use is to heat a pan or pail of water to boiling, and then carry it some distance from the fire. Now take the little flask con-

taining the gasoline and fat in the hand and hold it on the hot water. The gasoline will immediately begin to boil, and in a short time will mostly pass off into the air, leaving the fat and a little gasoline behind. Care must be taken that the gasoline does not boil over, for in that case some of the fat would be lost. If it shows any tendency to do this, lift the flask from the hot water a moment, and the boiling will stop. The water should not be allowed to cool too much before evaporating. The boiling gasoline will not burn the hand, as it boils at too low a temperature. The acetic acid is added to prevent the fat becoming gelatinous, as it frequently does without it. In creameries where steam is always to be had, a large number may be evaporated at once. Bore some holes in the top of a small closed box; these should be about the size of the bottom of the flasks. Place the flasks containing the gasoline and fat on top of these holes, and pass steam very slowly into the box through a rubber pipe. This is by far the easiest way, and requires only about five minutes for any number desired. The flow of steam must be under control, so that it may be stopped at any moment should the gasoline boil so fast as to be in danger of boiling over. Only a very little steam is required.

*Drying the Fat.*—The flasks containing the fat are placed on the shelf in the oven. The thermometer bulb should be on a level with the flasks. The oven is kept between 245 and 255 degrees Fahrenheit, and the flasks are dried at this temperature for the full time. If for more than five minutes the temperature should fall below 245, the flasks should be allowed to stay enough longer to make up for time thus lost. The flasks should drip into the measuring-tubes full ten minutes, with the temperature at the required height.

*Reading the Measuring-Tubes.*—After the fat is ready to measure, the tube is cooled down in the air, or, by taking care that none enters the tube, with water. As soon as the fat begins to grow opaque through solidification, the part of the tube containing fat is held clasped in the hand a moment until it clears up, when the reading is taken, which corresponds with the upper slightly curved surface of the fat. Considering 1 on the scale as 100, 2 as 200, 3 as 300, etc., each sub-division equals five. This is perhaps the best way to read the scale, as decimals are avoided.

*Cleaning the Apparatus.*—Always rinse out pipette No. 1 with water, and pipette No. 3 with gasoline, when through using them. To clean pipettes, thoroughly fill them with some of the caustic soda solution, taking care that none of it gets in the mouth, and let them stand some time. Then turn it back and rinse well with water. Pipettes Nos. 2 and 3 should be dried before again using for gasoline. The flasks should be cleaned in the same way whenever necessary. It must be remembered, however, that a film of fat is intended to remain on the inside, and as long as nothing but fat is present, cleaning is unnecessary. The tubes are cleaned carefully after each analysis by warming them, turning out the fat, and rinsing each one twice with gasoline while still warm. Dry before using.

*Using the Tables.*—Find the first two figures of the reading obtained from the scale in the left hand column headed c. c. Then pass horizontally towards the right to the column which has the third figure of the reading for its heading, and the per cent. of fat corresponding to the reading of the scale is found.

TABLE

FOR MILK, SKIMMED MILK, AND BUTTERMILK, CONTAINING FAT FROM .18 PER  
CENT. TO 8.56 PER CENT.

| c.c. | 0    | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|------|------|------|------|------|------|------|------|------|------|------|
| 0.1  | .18  | .20  | .22  | .24  | .26  | .27  | .29  | .31  | .33  | .35  |
| 0.2  | .36  | .38  | .40  | .42  | .    | .45  | .47  | .49  | .51  | .53  |
| 0.3  | .54  | .56  | .58  | .60  | .62  | .63  | .65  | .67  | .69  | .71  |
| 0.4  | .72  | .74  | .76  | .78  | .80  | .81  | .83  | .85  | .87  | .89  |
| 0.5  | .90  | .92  | .94  | .96  | .98  | 1.00 | 1.02 | 1.04 | 1.06 | 1.08 |
| 0.6  | 1.09 | 1.11 | 1.13 | 1.15 | 1.17 | 1.18 | 1.20 | 1.22 | 1.24 | 1.26 |
| 0.7  | 1.28 | 1.30 | 1.32 | 1.34 | 1.36 | 1.37 | 1.39 | 1.41 | 1.43 | 1.45 |
| 0.8  | 1.46 | 1.48 | 1.50 | 1.52 | 1.54 | 1.56 | 1.58 | 1.60 | 1.62 | 1.64 |
| 0.9  | 1.65 | 1.67 | 1.69 | 1.71 | 1.73 | 1.75 | 1.77 | 1.79 | 1.81 | 1.83 |
| 1.0  | 1.85 | 1.87 | 1.89 | 1.91 | 1.93 | 1.94 | 1.96 | 1.98 | 2.00 | 2.02 |
| 1.1  | 2.04 | 2.06 | 2.08 | 2.10 | 2.12 | 2.13 | 2.15 | 2.17 | 2.19 | 2.21 |
| 1.2  | 2.23 | 2.25 | 2.27 | 2.29 | 2.31 | 2.33 | 2.35 | 2.37 | 2.39 | 2.41 |
| 1.3  | 2.43 | 2.45 | 2.47 | 2.49 | 2.51 | 2.53 | 2.55 | 2.57 | 2.59 | 2.61 |
| 1.4  | 2.63 | 2.65 | 2.67 | 2.69 | 2.71 | 2.73 | 2.75 | 2.77 | 2.79 | 2.81 |
| 1.5  | 2.83 | 2.85 | 2.87 | 2.89 | 2.91 | 2.93 | 2.95 | 2.97 | 2.99 | 3.01 |
| 1.6  | 3.03 | 3.05 | 3.07 | 3.09 | 3.11 | 3.13 | 3.15 | 3.17 | 3.19 | 3.21 |
| 1.7  | 3.23 | 3.25 | 3.27 | 3.29 | 3.31 | 3.33 | 3.36 | 3.38 | 3.40 | 3.42 |
| 1.8  | 3.44 | 3.46 | 3.48 | 3.50 | 3.52 | 3.54 | 3.56 | 3.58 | 3.60 | 3.62 |
| 1.9  | 3.64 | 3.66 | 3.68 | 3.70 | 3.72 | 3.75 | 3.77 | 3.79 | 3.81 | 3.83 |
| 2.0  | 3.85 | 3.87 | 3.89 | 3.91 | 3.93 | 3.96 | 3.98 | 4.00 | 4.02 | 4.04 |
| 2.1  | 4.06 | 4.08 | 4.10 | 4.12 | 4.14 | 4.17 | 4.19 | 4.21 | 4.23 | 4.25 |
| 2.2  | 4.27 | 4.29 | 4.31 | 4.33 | 4.35 | 4.38 | 4.40 | 4.42 | 4.44 | 4.46 |
| 2.3  | 4.48 | 4.50 | 4.52 | 4.55 | 4.57 | 4.59 | 4.61 | 4.64 | 4.66 | 4.68 |
| 2.4  | 4.70 | 4.72 | 4.74 | 4.77 | 4.79 | 4.81 | 4.83 | 4.86 | 4.88 | 4.90 |
| 2.5  | 4.92 | 4.94 | 4.96 | 4.99 | 5.01 | 5.03 | 5.05 | 5.08 | 5.10 | 5.12 |
| 2.6  | 5.14 | 5.16 | 5.18 | 5.21 | 5.23 | 5.25 | 5.27 | 5.30 | 5.32 | 5.34 |
| 2.7  | 5.36 | 5.39 | 5.41 | 5.43 | 5.45 | 5.47 | 5.49 | 5.52 | 5.54 | 5.56 |
| 2.8  | 5.59 | 5.61 | 5.63 | 5.66 | 5.68 | 5.70 | 5.72 | 5.74 | 5.77 | 5.79 |
| 2.9  | 5.81 | 5.83 | 5.85 | 5.88 | 5.90 | 5.92 | 5.94 | 5.97 | 5.99 | 6.01 |
| 3.0  | 6.04 | 6.06 | 6.08 | 6.11 | 6.13 | 6.15 | 6.17 | 6.20 | 6.22 | 6.24 |
| 3.1  | 6.27 | 6.29 | 6.31 | 6.34 | 6.36 | 6.38 | 6.40 | 6.43 | 6.45 | 6.47 |
| 3.2  | 6.50 | 6.52 | 6.54 | 6.57 | 6.59 | 6.62 | 6.64 | 6.66 | 6.68 | 6.70 |
| 3.3  | 6.73 | 6.75 | 6.77 | 6.80 | 6.82 | 6.85 | 6.87 | 6.89 | 6.92 | 6.94 |
| 3.4  | 6.97 | 6.99 | 7.01 | 7.04 | 7.07 | 7.09 | 7.12 | 7.14 | 7.16 | 7.18 |
| 3.5  | 7.20 | 7.22 | 7.25 | 7.28 | 7.31 | 7.33 | 7.35 | 7.38 | 7.41 | 7.43 |
| 3.6  | 7.45 | 7.47 | 7.49 | 7.52 | 7.54 | 7.57 | 7.59 | 7.61 | 7.64 | 7.66 |
| 3.7  | 7.69 | 7.71 | 7.74 | 7.76 | 7.79 | 7.81 | 7.83 | 7.86 | 7.88 | 7.91 |
| 3.8  | 7.94 | 7.96 | 7.99 | 8.01 | 8.03 | 8.06 | 8.08 | 8.11 | 8.14 | 8.17 |
| 3.9  | 8.19 | 8.22 | 8.25 | 8.27 | 8.29 | 8.31 | 8.34 | 8.36 | 8.38 | 8.41 |
| 4.0  | 8.43 | 8.46 | 8.48 | 8.51 | 8.53 | 8.56 |      |      |      |      |

CREAM, 15 PER CENT. TO 45.60 PER CENT.

[illegible]

**A SCHEME FOR THE SEPARATION AND DETECTION OF AL, CR, FE, CO, NI, MN, ZN, BA, CA, SR, MG, IN THE PRESENCE OF PHOSPHORIC, ARSENIC, OXALIC, BORIC, SILICIC, HYDROFLUORIC, ACETIC, TARTARIC ACIDS AND ORGANIC MATTER.**

By J. S. C. WELLS, PH.D., AND H. T. VULTE, PH.D.\*

It is a well-known fact that the usual separation with ammonium hydrate, chloride and sulphide fail in the presence of any of the above-mentioned acids. The various methods in use are long, and in most cases inaccurate. In presenting the following, we have tried to cover every point of importance, and wherever possible have used quantitative methods for the sake of accuracy.

The scheme has been given a careful trial, and seems to meet all requirements.

If a solution containing the before-mentioned acids and bases is made alkaline with ammonium hydrate, the following is likely to occur :—

| H <sub>3</sub> PO <sub>4</sub>                              | ppts. | Al   | Cr | Fe(ic) | Co | Ni | Mn | Zn | Ba | Sr | Ca | Mg |
|---|-------|--|----|--------|----|----|----|----|----|----|----|----|
| H <sub>3</sub> BO <sub>3</sub>                              | "     | "  | "  | "      | "  | "  | "  | "  | "  | "  | "  | "  |
| H <sub>2</sub> SiO <sub>3</sub>                             | "     | "  | "  | "      | "  | "  | "  | "  | "  | "  | "  | "  |
| H F   | "     | "  | "  | "      | "  | "  | "  | "  | "  | "  | "  | "  |
| H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>                | "     | chiefly  |    | "      | "  | "  | "  | "  | "  | "  | "  | "  |
| H <sub>3</sub> AsO <sub>4</sub>                             | "     | Fe(ic) and Mg  |    | "      | "  | "  | "  | "  | "  | "  | "  | "  |
| H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> | }     | prevent precipitation of Al, Cr, Fe, if boiling and neutral, HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub><br>throws down Al, Cr and Fe as Basic Acetates. |    |        |    |    |    |    |    |    |    |    |
| HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>               |       |  |    |        |    |    |    |    |    |    |    |    |
| Organic Matter  |       |  |    |        |    |    |    |    |    |    |    |    |

To test for the presence of these compounds three small portions of the main solution are taken as follows :—

Part I. Add HNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub> Mo O<sub>4</sub> a yellow cryst. ppt. indicates phosphates, if heated gently a yellow colour or ppt. indicates silicates and arsenates.

Part II. Add H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> and NH<sub>4</sub>OH in excess a gelatinous ppt. indicates phosphates, borates, etc.

Part III. Add conc. H<sub>2</sub>SO<sub>4</sub>, and evaporate to dryness; a carbonaceous residue indicates organic acids or matter.

All the acids mentioned, except phosphoric, boric and arsenic, may be removed by evaporation with HNO<sub>3</sub> and ignition. Borates are soluble in a considerable excess of ammonium chloride, and give no trouble.

Arsenates are removed by reduction with SO<sub>2</sub> and precipitation as As<sub>2</sub>S<sub>3</sub> by H<sub>2</sub>S. This should be done before adding HNO<sub>3</sub>.

After making these tests, return to main solution.

Boil out H<sub>2</sub>S. Add a few drops HNO<sub>3</sub> (Note 1). If H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or organic matter is present evaporate to dryness and ignite gently. If not, evaporate, but do not ignite. Treat residue with HCl (conc.), dilute with H<sub>2</sub>O and boil; it dissolves wholly or leaves a white residue of SiO<sub>2</sub>. Filter. To filtrate add NH<sub>4</sub>Cl and NH<sub>4</sub>OH in slight excess, heat gently and filter quickly, wash ppt. A with hot water. To filtrate add (NH<sub>4</sub>)<sub>2</sub>S slight xs heat, filter and wash ppt. B. Examine filtrate for the alkalies and alkaline earths. Transfer ppts. A and B to a porcelain dish and digest with a little (NH<sub>4</sub>)<sub>2</sub>S. (Note 2), filter and wash with H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>S.

\* *School of Mines Quarterly*, X., 3.

Filt. Residue  $\text{Al}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ ,  $\text{FeS}$ ,  $\text{Al}_2(\text{PO}_4)_3$ ,  $\text{Cr}_2(\text{PO}_4)_3$ ,  $\text{Ba}_3(\text{PO}_4)_2$ ,  $\text{Sr}_3(\text{PO}_4)_2$ ,  
 $(\text{NH}_4)_3\text{PO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{NH}_4$ ,  $\text{Mg}(\text{PO}_4)$ ,  $\text{MnS}$ ,  $\text{ZnS}$ ,  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{S}$ .  
 $(\text{NH}_4)_2\text{S}$  Treat with cold very dilute  $\text{HCl}$  sp. gr. 1.05, filter and wash.  
 Reject

|   |  |  |   |
|---|--|--|---|
| Residue<br>$\text{NiS} + \text{CoS} + \text{S}$<br>Test a portion<br>in Borax Bead<br>Blue = Co<br>Brown = Ni<br>If blue, diss.<br>in $\text{Cl}$ evap. to ex-<br>pel xs acids and<br>$\text{Cl}$ , dil. + $\text{H}_2\text{O}$<br>nearly neutralise<br>+ $\text{KOH}$ add<br>$\text{KCY}$ until ppt.<br>formed is diss.,<br>boil for 4 or 5<br>minutes, cool,<br>add large xs<br>$\text{KOH} + \text{Br}$<br>water<br>a black ppt.<br>$\text{Ni}_2(\text{OH})_6$ wash<br>with very dilute<br>$\text{NH}_4\text{OH}$ to re-<br>move last trace<br>of Co test in Bo-<br>rax bead.<br>Brown Bend Ni | Filtrate<br>Contains Fe, Al, Cr, Zn + Mn as chlorides, and Al, Cr, Ba,<br>Sr, Ca, Mg as Phosphates.<br>Boil out $\text{H}_2\text{S}$ , dilute and make alkaline with $\text{Na}_2\text{CO}_3$ , add<br>Bromine water and boil until Cr is all oxidised and Br.<br>removed. Filter. |  |   |
|   | Filtrate<br>$\text{Na}_2\text{CrO}_4$<br>Acidify<br>with<br>$\text{H}\bar{\text{A}}$ .<br>Test for<br>Cr with<br>$\text{BaCl}_2$<br>yellow<br>ppt.<br>$\text{BaCrO}_4$<br>= Cr.<br>(Note 3.)   | Ppt. $\text{Al}_2(\text{OH})_6$ , $\text{Al}_2(\text{PO}_4)_3$ , $\text{Fe}_2(\text{OH})_6$ , $\text{Fe}_2(\text{PO}_4)_3$ , Ba, Sr,<br>Ca, Mg Phos. Zn + Mn Basic Carbs. Diss. in<br>least possible quantity of dil. $\text{HCl}$ and add<br>$\text{Fe}_2\text{Cl}_6$ until a few drops of the sol. give a yel-<br>low or red ppt. with $\text{NH}_4\text{OH}$ . (Note 4.) Nearly<br>neutralise with $\text{Na}_2\text{CO}_3$ , dilute and add xs of<br>$\text{Na}\bar{\text{A}}$ . Boil and filter hot. Wash ppt. with<br>boiling $\text{H}_2\text{O}$ . |   |
|   |  | Ppt.<br>Fe and Al as Phos-<br>phates and Basic Ace-<br>tates add $\text{KOH}$ and<br>boil.   | Filtrate  .<br>Zn Mn Ba Sr Ca Mg as<br>acetates or chlorides<br>add $\text{NH}_4\text{Cl}$ $\text{NH}_4\text{OH} +$<br>$(\text{NH}_4)_2\text{S}$ . Filter and wash.   |
|   |  | Ppt.<br>$\text{Fe}_2(\text{OH})_6$<br>$\text{Fe}_2(\text{PO}_4)_3$   | Filt.<br>Add $\text{HCl}$<br>to acid re-<br>action and<br>then make<br>alk. with<br>$(\text{NH}_4)_2\text{CO}_3$<br>white ppt.<br>$\text{Al}_2(\text{OH})_6$<br>and<br>$\text{Al}_2(\text{PO}_4)_3$ .       |
|   |  | Ppt.<br>$\text{ZnS} +$<br>$\text{MnS}$ .   | Filtrate Ba,<br>Ca, Sr, Mg<br>acetates or<br>chlorides.<br>Examine in<br>usual manner.  |
|   |  |  | Treat with $\text{H}\bar{\text{A}}$ .   |
|   |  | Res<br>$\text{ZnS}$<br>Treat on<br>charcoal<br>with<br>$\text{Co}(\text{NO}_3)_2$<br>green<br>mass Zn.   | Solution<br>$\text{Mn}\bar{\text{A}}_3$ add<br>$\text{KOH}$ white ppt.<br>turning brown<br>in the air, fuse<br>with $\text{Na}_2\text{CO}_3$ .<br>Green mass<br>$\text{Na}_2\text{MnO}_4$ indi-<br>cates Mn |

## NOTES.

I.  $\text{HNO}_3$  is added to oxidize Fe and destroy  $\text{H}_2\text{C}_2\text{O}_4$ , organic acids and matter.

II.  $\text{NH}_4\text{OH}$  ppt. Fe, Al, Cr as hydrates and phosphates, and the other metals of the group as phosphates, if they are in combination with that acid, it also ppt. all of the phosphates of the alkaline earths that may be present.

Ppt. A is treated with  $(\text{NH}_4)_2\text{S}$  to convert the phosphates (except those of Al, Cr, Ba, Sr, Ca and Mg) into sulphides, the  $\text{H}_3\text{PO}_4$  is taken up by the  $\text{NH}_4\text{OH}$  in a soluble form and filtered off, thereby making a partial separation of the phosphoric acid.

III. A pink or green colouration may be caused by the oxidation of Mn to permanganate or manganate, neither interferes with the  $\text{BaCl}_2$  test.

IV. Ferric salt is added to carry down the phosphoric acid, as  $\text{Fe}_3(\text{PO}_4)_2$ , white solution must be alkaline with  $\text{NH}_4\text{OH}$ , when all the  $\text{H}_3\text{PO}_4$  is pptd. the  $\text{NH}_4\text{OH}$  brings down the yellow or brown  $\text{Fe}_2(\text{OH})_6$ .

V. Instead of scheme as above the following may be used :—

Filt. containing Mn, Zn, Ba, Sr, Ca, Mg as acetates or chlorides add Br and boil as long as a black ppt. is formed and colour of Br remains; filter.

|                                       |  |   |
|---------------------------------------|--|---|
| Ppt.                                  | Filt. Zn, Ba, Sr, Ca, Mg acetates or chlorides.              |   |
| $\text{MnO}_2\cdot\text{H}_2\text{O}$ | Warm, pass a rapid current of $\text{H}_2\text{S}$ , filter. |   |
| test in                               | $\text{ZnS}$   | Filt.   |
| $\text{Na}_2\text{CO}_3$              | white, if  | Boil out $\text{H}_2\text{S}$ , and proceed as usual. |
| bead.                                 | dark coloured  |   |
|                                       | test on char-  |   |
|                                       | coal with  |   |
|                                       | $\text{Co}(\text{NO}_3)_2$ .                                 |   |

## ON THE DENSITIES AND REFRACTIVE INDICES OF CERTAIN OILS.

By J. H. LONG.

(Continued from page 178.)

*Mustard Oil.*

The oil of black mustard may be classed among the cheaper oils, and when properly refined has numerous uses. I have examined two samples of known purity, and a third prepared from one of these by partial saponification. The first two had been well refined, and were almost entirely free from the odour of the volatile oil.

No. 2. A sample obtained in Chicago.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 4.0° | .9222 | 14.5° | 1.4769 |
| 19.1 | .9122 | 17.5  | 1.4751 |
| 34.0 | .9026 | 20.5  | 1.4739 |
| 48.6 | .8932 | 22.5  | 1.4732 |
|      |       | 24.5  | 1.4724 |
|      |       | 28.9  | 1.4706 |
|      |       | 35.0  | 1.4683 |
|      |       | 40.0  | 1.4663 |

No. 15. Oil refined from the above by treatment with a 1 per cent. solution of potassium hydrate.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 1.5° | .9251 | 14.8° | 1.4771 |
| 16.6 | .9149 | 19.3  | 1.4749 |
| 33.6 | .9037 | 21.3  | 1.4739 |
| 47.4 | .8946 | 23.3  | 1.4729 |
|      |       | 25.8  | 1.4720 |
|      |       | 31.3  | 1.4700 |
|      |       | 34.3  | 1.4688 |
|      |       | 37.3  | 1.4677 |

No. 17. A sample obtained from a New York importer.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 1.7° | .9239 | 15.3° | 1.4759 |
| 18.6 | .9128 | 19.3  | 1.4743 |
| 36.0 | .9014 | 21.3  | 1.4736 |
| 45.8 | .8948 | 23.8  | 1.4726 |
|      |       | 27.3  | 1.4712 |
|      |       | 31.8  | 1.4694 |
|      |       | 36.8  | 1.4674 |
|      |       | 39.3  | 1.4665 |

The temperature coefficients are nearly as observed in the other oils.

*Peanut Oil.*

One sample of oil, partially refined, was examined, with these results.

No. 19.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 3.2° | .9309 | 15.8° | 1.4736 |
| 17.9 | .9186 | 19.8  | 1.4718 |
| 34.4 | .9074 | 23.3  | 1.4704 |
| 47.7 | .8984 | 25.3  | 1.4696 |
|      |       | 28.3  | 1.4684 |
|      |       | 34.3  | 1.4661 |
|      |       | 39.2  | 1.4641 |

While the change in the density is comparatively rapid between the lowest temperatures, it amounts to .00068 for each degree between the mean temperatures, that is, the rate is about as before given. The variation in the refractive index is normal.

*Castor Oil.*

The following results were obtained by examination of a sample of well-refined cold-pressed oil.

No. 3.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 4.0° | .9695 | 14.4° | 1.4831 |
| 7.1  | .9675 | 18.4  | 1.4806 |
| 18.0 | .9602 | 20.4  | 1.4790 |
| 32.5 | .9505 | 22.9  | 1.4781 |
| 46.8 | .9410 | 25.4  | 1.4771 |
|      |       | 28.4  | 1.4759 |
|      |       | 33.9  | 1.4741 |
|      |       | 37.3  | 1.4728 |

*Lard Oil.*

A sample of pure oil, pressed in Chicago, was examined, and gave these figures. As it became thick at the lowest temperature, the density determination at that point is probably not quite accurate.

No. 13.

| T.   | D.    | T.    | N.     |
|------|-------|-------|--------|
| 1.8° | .9287 | 20.3° | 1.4685 |
| 15.5 | .9154 | 24.3  | 1.4669 |
| 32.5 | .9036 | 27.3  | 1.4657 |
| 48.5 | .8926 | 29.3  | 1.4649 |
|      |       | 32.3  | 1.4637 |
|      |       | 36.3  | 1.4622 |
|      |       | 39.2  | 1.4612 |



In order to compare the values for the different oils with each other, as well as with similar data obtained by other observers, I have calculated from the above direct observations the numbers in the tables below. In most cases the curve representing the variations in specific gravity is nearly a straight line, and without introducing appreciable error it can be taken as linear between the intermediate temperatures. Assuming these points as correctly determined, I have interpolated values from 18° to 25° and for 30° and 35°.

By means of carefully drawn curves I have interpolated, from the direct determinations of  $N$ , the values for the same degrees of temperature. The numbers thus obtained are undoubtedly as accurate and satisfactory as could be obtained by a laborious method of calculation. Finally, I have calculated the "specific refractive energy,"  $\frac{N-1}{D}$ , and give these values in another column.

(To be continued.)

## REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

A SOURCE OF ERROR IN THE SEPARATION OF A SMALL QUANTITY OF MANGANESE FROM A LARGE AMOUNT OF LIME BY AMMONIUM SULPHIDE. BY L. BLUM. (*Zeits. f. Anal. Chem.* 28, 454.)—In the precipitation of manganese by ammonium sulphide, Fresenius recommends that in all cases at least twenty-four hours, and in the presence of very small quantities of manganese, forty-eight hours should elapse before filtration. The author finds that with much lime and little manganese, a crystalline precipitate of calcium thiosulphate is deposited; to avoid this he filters off at once after a good boiling up.

H. D. R.

THE ESTIMATION OF NITRIC NITROGEN BY KJELDAHL'S METHOD. BY DR OTTO FOERSTER (*Zeits. f. Anal. Chem.* 28, 422).—By the application of phenol-sulphonic acid to the estimation of nitrogen by Kjeldahl's method in nitrates, the results are obtained slightly low, because on heating some of the nitric acid volatilises without having combined with the phenol. This loss may be prevented by the use of a second substance, forming a less volatile combination with the nitric acid. The author has made many experiments with a phenol-sulphonic acid solution, containing varying quantities of phenol, both with and without reducing agent, preferably sodium thiosulphate, which with the nitric and sulphuric acids forms "Lead Chamber Crystals." Another source of error is due to the use of india-rubber connexions, there being a loss in his experiment of 2 m. grs. of nitrogen for each gram. of nitre. This is avoided by the use of an apparatus containing the standard acid, consisting of 5 bulbs (described and figured in Fresenius' "Quantitative Analysis," 6th edition, l. 224), into which the tube from the distillation flask is directly led. With this apparatus, and by the use of a phenol-sulphonic acid solution containing 5-6 per cent. phenol, of which 30 c.c. are used for each grm. of nitre, and by the addition of about 1 grm. sodium thiosulphate, the author finds results with potassium nitrate very closely agreeing with the theory. H. D. R.

THE ESTIMATION OF THE EXTRACT IN WINE BY THE INDIRECT METHOD. BY E EGGER (*Zeits. f. Anal. Chem.* 28, 396).—A commission appointed in 1874 to examine the methods of Wine Analysis, give the following instruction for taking the "extract": "50 c.c. of wine, measured at 15° C. are evaporated in a platinum basin (80 m.m. across, 50 m.m. high, holding 75 c.c., and weighing about 20 grms.) on a water bath, and the residue dried for two and a half hours in a water oven. Of wines rich in sugar (*i.e.*, containing .5 grm. sugar in 100 c.c.), a quantity suitably diluted is taken, so that from 1.15 grms. are left."

Both Schultze (*Zeits. f. Anal. Chem.* 19, 104) and Hager (*ibid.* 17, 502) give tables for the calculation of the extract from the density of the wine from which the alcohol has been boiled off.

The author has compared in 150 experiments the results obtained directly with those calculated from both tables, with the following results:—

| Difference between numbers calculated and those found. | Schultze.           | Hager.            |
|--|---------------------|-------------------|
| under .2 per cent.                                     | in 132 experiments. | in 6 experiments. |
| .2 — .5     "  | 18     "            | 115     "         |
| over .5     "  | —     "             | 29     "          |

He therefore gives the preference to Schultze's tables; the low results given by the uses of Hager's figures being due to the fact that he dried the malt extract (which he used in the preparation of the solutions from which his tables were calculated) at 110° C.

H. D. R.

THE ESTIMATION OF NITROGEN BY KJELDAHL'S METHOD. BY F. MARTINOTTI (*Zeits. f. Anal. Chem.* 28, 415).—From comparative analyses with manures, the author concludes that in the absence of nitrates the Kjeldahl method is preferable to the soda-lime method. He considers the use of mercury, and in many cases potassium permanganate, unnecessary, and finds that in their absence the distillation is more regular. In the presence of nitrates he does not recommend the use of the Kjeldahl-Jodlbauer method, but prefers to first reduce the nitrate by heating with concentrated hydrochloric acid and ferrous chloride.

H. D. R.

PURIFICATION OF LITMUS. BY DR. OTTO FOERSTER (*Zeits. f. Anal. Chem.* 28, 428).—Dr. Foerster recommends, as an indicator in Kjeldahl's method, a solution of 9 grms. litmus and 1 grm. malachite green in 1 litre of alcohol. Commercial litmus is extracted with ordinary alcohol in the cold, then digested with water, the solution filtered and evaporated; the residue is again dissolved in water, filtered, and the filtrate precipitated with absolute alcohol, to which some acetic acid is added. The precipitate is collected on a filter and washed with alcohol, whereby a violet, fluorescent colouring matter is separated; the residue is again dissolved in water and precipitated, filtered, and washed as before. By the second repetition only a small quantity of the colouring matter is separated. The precipitate is stirred up with alcohol to remove the acetic acid, and then again dissolved in water and the solution filtered. The colouring matter finally precipitated with slightly ammoniacal alcohol, collected on a filter, washed with strong alcohol and dried, is used to make up the solution.

H. D. R.

PURITY OF QUININE SULPHATE. J. E. DE VRY. *Nederl. Tydschr. v. Pharmacie*, etc.

—1. The chromate test; two grammes of quinine sulphate are dissolved in 80 c.c. of boiling water and mixed with a solution of .55 grammes of potassic chromate. After the liquid has cooled down until 15°C., the liquid is filtered off from the precipitated quinine chromate. Solution of caustic soda is now added until the liquid is distinctly alkaline to phenol-phthalein paper. If the sample is practically pure, viz., contains no more than .5 per cent. of other alkaloids, the liquid will remain clear; but if large amounts of impurities are present, the liquid will get more or less turbid. Although the process does not lay claim to *quantitative* accuracy, still, with a little practice, a fair idea may be got about the percentage of impurities. The quinine may be readily recovered from the collected chromate by dissolving the mass in boiling water and precipitating with soda ley. 2. The optical test; two grammes of the sample are dissolved in 80 c.c. of hot water and mixed with a hot solution of two grammes of Rochelle salts. After a little while, the tartrate begins to crystallize out. After standing for a day, the precipitate is filtered off, washed and air dried. The molecular rotation of the tartrate  $[A_D]$  0 of a sample submitted to the author was 209.33, showing it to consist of 92.34 QT and 7.56 C<sup>st</sup>T, which, calculated on original sample, corresponds with 92.62 quinine sulphate and 7.38 cinchonidine ditto. If, as sometimes happens, the sample has an alkaline reaction, it must first be neutralised with dilute sulphuric acid; otherwise a basic tartrate will be obtained, which gives too low a polarisation. For the detection of large quantities of cinchonidine, the ether test answers well enough, providing the ether is absolutely free from alcohol. A sample from a well known French firm was guaranteed not to give any separation on agitating with alkali and ether. The author really found such to be the case when he used common ether containing alcohol, but by using pure ether the impurity was at once detected.

L. DE K.

NEW TEST FOR ANTIARINE. WEFERS BETTINK. *Nederl. Tydschr. v. Pharmacie* etc., April, 1889.—The author discovered a delicate reaction for this formidable arrow poison. If 1 c.c. of a 5 per cent. solution of sodium carbonate is boiled with three drops of a cold saturated solution of picric acid, the yellow colour does not perceptibly change. If, however, as little as .0001 gramme of antiarine is added, the colour turns orange-red. The colour is not produced by such glucosides as aesculine, amygdaline, phloroglucine, digitaline, and picrotoxine. This test, in conjunction with physiological experiments, enables us to recognise the poison. A few milligrammes of antiarine, when injected in the blood, will kill dogs or rabbits in a few seconds.

L. DE K.

ESTIMATION OF CANTHARIDIN. J. B. NAGELVOORT. *Nederl. Tydschr. v. Pharmacie* etc., July, 1889.—The best method as yet known, originated by Greenish, gives certainly fair results in experienced hands, but, it cannot be denied it is a most troublesome and costly process. For instance, 10 grammes of the cantharides must be exhausted with benzol to remove the fat, and frequently as much as 200 c.c. of this fluid will be required. The exhausted residue must be digested in soda ley, and then dried, when it will be often found almost impossible to powder. The cantharadin is dissolved out by

ether and chloroform, and finally purified by alcohol. Now, as it is very perceptibly soluble in benzol and in alcohol, the volumes of these fluids must be carefully noted and corrections must be applied, so that sometimes one half of the cantharidin found is made up by allowances. The author now proposes the following process: 10 grammes of the cantharides are moistened with a 10 per cent. soda ley, and put in a warm place for six hours. The mass is now acidified with hydrochloric acid, transferred to a Soxhlet's tube and fully exhausted by means of chloroform (about 50 c.c.). After evaporating off the chloroform, the residue is freed from fat by means of carbon disulphide, and then redissolved in chloroform. The liquid is filtered off and evaporated to dryness at  $79.5^{\circ}\text{C}$ ., when the cantharidin may be weighed.

L. DE K.

### REVIEWS.

THE CHEMICAL ANALYSIS OF IRON: A COMPLETE ACCOUNT OF ALL THE BEST KNOWN METHODS FOR THE ANALYSIS OF IRON, STEEL, PIG-IRON, IRON ORE, LIMESTONE, SLAG, CLAY, SAND, COAL, COKE, AND FURNACE AND PRODUCER GASES. By ANDREW ALEXANDER BLAIR. London: Whittaker and Co., White Hart Street, Paternoster Square.

THE immense mass of matter which has appeared on the subject of the analysis of iron and of the various materials employed in its manufacture, or produced in the course thereof, has been so widely distributed through all sorts of periodicals, that a good compilation like that now under consideration is really a most serviceable book. As might have been expected from the author's antecedents—he having (after graduating in the United States Naval Academy in 1866) been chief chemist to the States Board appointed to test iron, steel, and other metals in 1875, and subsequently chief chemist to the United States Geological Survey—the work is something more than a mere compilation. With very few exceptions the descriptions are the results of the author's own experience in the use of the particular methods detailed, while the points specially insisted upon are those that seemed to him to be specially important when practically performing the processes in question. In the preface the author seems to indicate that “works” chemists are not better treated in America than they are with us, because he says:—“Many of the special forms of apparatus are of my own contrivance; they have proved extremely useful to me, and I hope may facilitate in some cases the work of iron chemists, to whom often very little is given and of whom very much is required.” Like most of the American books that have lately appeared, the style both of printing and illustrations are admirable; the former is very easy to read, and the latter are plain and sufficiently numerous; we should be inclined to think that there will be very few analysts interested in the subject that will not provide themselves with a copy of the book. It is not, however, to the specialist only that the work will be useful, because it is so shortly and yet lucidly written as to be just the sort of book that a general chemist would keep handy in the event of his being called upon to engage in such analysis; when it would certainly come in very useful and save much loss of time in hunting through one's library.

**A TREATISE ON MANURES ; OR, THE PHILOSOPHY OF MANURING : A PRACTICAL HANDBOOK FOR THE AGRICULTURIST, MANUFACTURER, AND STUDENT. By A. B. GRIFFITHS, Ph.D., F.R.S.E., etc. London : Whittaker and Co., White Hart Street, Paternoster Square.**

THIS is one of a set of handy books now being published by Messrs. Whittaker under the name of the "Specialist's Series." It may be at once said that it meets a decided want. It is lucidly written, and at the same time is sufficiently popular to be appreciated by the class of men to whom it ought to be most vitally interesting, viz., the farmers. It is only to be hoped that they will, as a body, carefully peruse it ; but, in his preface, the author does not seem to be very sanguine on this point, because he says :—"Farmers as a class hold most tenaciously to their old customs, and are most jealous of innovations. They remember the days of prosperity, and, hoping for their return, ignore the immense advance in every other industry, and continue in the old routine to compete with the foreign agriculturist in the production of cereals, while enormous quantities of commodities are imported that could be more advantageously produced by themselves. In the words of an anonymous writer in a weekly paper : 'Orthodoxy is an institution of a past generation, and no more adapted to the present times than her contemporaries the flail or the spinning-wheel. She cannot even be defended on the ground of continuing to supply a required need in the absence of something better. She stands proved a complete failure, and, as such, should be blotted out. She impedes progress ; she insists on the cultivation of crops that of foreknowledge will result in loss ; and she admits of no departure to suit existing circumstances. . . . Can nothing be said in favour of Orthodoxy ? Is there no favourable aspect ? No, not one ! She is neither the friend of the landlord, tenant, nor labourer. Many of the natural advantages which we formerly possessed as a nation have been taken from us by that great leveller, Steam, which brings products to our shores and equalises the advantages which one nation formerly enjoyed over another. We cannot retrograde to the blissful past ; therefore the farmer must alter his system of sowing, manuring, etc., to suit the changed condition of things. What is the use of still continuing a system that does not pay ? Self-interest, therefore, should lead farmers to throw away their old prejudices, and listen more attentively to the teaching of science rather than look for help to politicians.'"

The book begins with a short historical account of the progress of agriculture, and then takes up the constituents of plants and the physiology of their nutrition. In urging the necessity of manuring, the author introduces a pungent little illustration by telling the story of the priest, who, having been called to pray over the barren fields of his parishioners, and having passed from one enclosure to another, at the same time pronouncing his benediction over each, came to a most unpromising case. He surveyed the sterile acres in despair. "Ah," said he, "brethren, no use to pray here—this needs manure." While, however, thus urging the use of manures, the author carefully distinguishes between their use and abuse, because we find him quoting the following valuable words of Stutzer :—"The manure produced on the farm is in very few cases sufficient to supply the cultivated plant with the nitrogen it requires to produce crops securing the highest possible clear profit. The practical farmer must therefore have recourse to artificial manure . . . . Even with this high farming, there are fields in which

the plants may be brought to a richer development by an increase of manure, and yet this increased manuring is not advisable as soon as it 'does not pay.' It is not the aim of the farmer to produce the greatest crops irrespective of profit or loss, but to realise the utmost clear profit; therefore more manure must not be used than is profitable."

Having discussed all the varieties of natural and artificial manures, and gone thoroughly into the constituents and modes of manufacture of the latter, the author makes a special study of the manurial value of ferrous sulphate, a subject with which his name has been previously identified. Then follows a chapter upon Ville's system of manuring, and the whole ends with directions for the analysis and valuation of fertilizers. There is no doubt that this work is one of the best that has yet been produced at a moderate price, so as to be within the reach of all.

EXAMINATION OF WATER FOR SANITARY AND TECHNICAL PURPOSES. By HENRY LEFFMANN, M.D., and WILLIAM BEAM, M.A. Philadelphia: P. Blakiston, Son and Co.

THIS little book contains within 100 pages full instructions for the sanitary and quantitative analysis of water, and as such, it can, of course, be little more than a reproduction of well-known matter. It is probable that such a publication may fill a void in American chemical literature, but, over here, there is really very little opening for the *brochure*, because the ground is already fully covered by Wanklyn, Fox, and many others. The mineral quantitative part is based on Fresenius, and we suppose that a better model could not have been chosen. The sanitary part is, with some slight deviations, practically the instructions for water analysis approved by the Society of Public Analysts, and published in our columns some years ago. The two main points of difference consist in the hardness estimation and in the nitrates and nitrites. In the former case the time-honoured soap test is given up, and Mr. Hehner's method (with sodium carbonate and sulphuric acid) is substituted. Whether this is a good departure or not, it will certainly be submitted to a good deal of conservative criticism. In the latter case all the usual processes in common use are given up, and the methods recommended are the purely colorimetric ones first brought into notice (if we are not mistaken) in our columns by Mr. Percy Smith. Here we think there is the decided advantage that the authors obtain a separate estimation of the nitrogen as nitrates and that as nitrites, and so undoubtedly gain more information as to the actual stage of oxidation. As these processes have never obtained a firm hold in this country, it will be interesting to some of our readers to extract them here, and thus give an idea of the general style of the book.

#### NITROGEN AS NITRATES.

##### SOLUTIONS REQUIRED:—

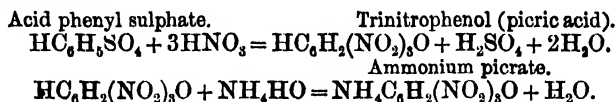
*Acid Phenyl Sulphate*.—18.5 c.c. of strong sulphuric acid are added to 1.5 c.c. of water and 3 grams. of pure phenol. Preserve in a tightly-stoppered bottle.

*Standard Potassium Nitrate*.—0.722 gram. of potassium nitrate, previously heated to a temperature just sufficient to fuse it, is dissolved in water, and the solution made up to 1,000 c.c. 1 c.c. of this solution will contain .0001 grm. of nitrogen.

## ANALYTICAL PROCESS :—

A measured volume of the water is evaporated just to dryness in a platinum or porcelain basin. 1 c.c. of the acid phenyl sulphate is added and thoroughly mixed with the residue by means of a glass rod. 1 c.c. of water is added, three drops of strong sulphuric acid, and the dish gently warmed. The liquid is then diluted with about 25 c.c. of water, ammonium hydroxide added in excess, and the solution made up to 100 c.c.

The reactions are :—



The ammonium picrate imparts to the solution a yellow colour, the intensity of which is proportional to the amount present.

Five c.c. of the standard solution of potassium nitrate is now similarly evaporated in a platinum basin treated as above, and made up to 100 c.c. The colour produced is compared to that given by the water ; and one or the other of the solutions diluted until the tints of the two agree. The comparative volumes of the liquids furnish the necessary data for determining the amount of nitrate present, as the following example will show :—

Five c.c. of standard nitrate is treated as above, and made up to 100 c.c.

$$\begin{array}{r} \cdot 0001 \\ 5 \\ \hline \cdot 0005 \text{ gram. N per 100 c.c.} \\ 10 \\ \hline \cdot 0050 \text{ „ „ 1,000 „} \end{array}$$

Suppose 100 c.c. water similarly treated is found to require dilution to 150 c.c. before the tint will match that of the standard ; then

$$100 : 150 :: \cdot 005 : \cdot 0075$$

i.e., water contains 7·5 milligrams. of nitrogen as  $\text{NO}_3$  per litre.

The ammonium picrate solution keeps very well, especially in the dark. A good plan, therefore, is to make up a standard solution equivalent to, say, ten milligrams. of nitrogen as nitrate per litre, to which the colour obtained from the water may be directly compared.

The results obtained by this method are quite accurate. Care should be taken that the same quantity of acid phenyl sulphate is used for the water and for the comparison liquid, otherwise different tints instead of depths of tints are produced.

With subsoil and other waters probably containing much nitrates, 10 c.c. of the sample will be sufficient for the test, but with river and spring waters, 25 to 100 c.c. may be used. When the organic matter is sufficient to colour the residue, it will be well to purify the water by addition of alum and subsequent filtration, before evaporating.

## NITROGEN AS NITRITES.

## SOLUTIONS REQUIRED :—

*Naphthylammonium Chloride.*—Saturated solution in water free from nitrites. It should be colourless ; a small quantity of animal charcoal allowed to remain in the bottle will keep it in this condition.

*Para-amido-benzene-sulphonic Acid [Sulphanilic Acid].*—Saturated solution in water free from nitrites.

*Hydrochloric Acid.*—25 c.c. of concentrated pure hydrochloric acid added to 75 c.c. water free from nitrites.

*Standard Sodium Nitrite.*—0.275 gram. pure silver nitrite is dissolved in pure water, and a dilute solution of pure sodium chloride added until the precipitate ceases to form. It is then diluted with pure water to 250 c.c., and allowed to stand until clear. For use 10 c.c. of this solution are diluted to 100 c.c. It is to be kept in the dark.

One c.c. of the dilute solution is equivalent to .00001 gram. nitrogen.

The silver nitrite is prepared thus: A hot concentrated solution of silver nitrate is added to a concentrated solution of the purest sodium or potassium nitrite available, filtered while hot and allowed to cool. The silver nitrite will separate in fine needle-like crystals, which are freed from the mother liquor by filtration by the aid of a filter-pump. The crystals are dissolved in the smallest possible quantity of hot water, allowed to cool and again separated by means of the pump. They are then thoroughly dried in the water-bath, and preserved in a tightly-stoppered bottle away from the light. Their purity may be tested by heating a weighed quantity to redness in a tarred porcelain crucible and noting the weight of the metallic silver. 154 parts of  $\text{AgNO}_3$  leave a residue of 108 parts Ag.

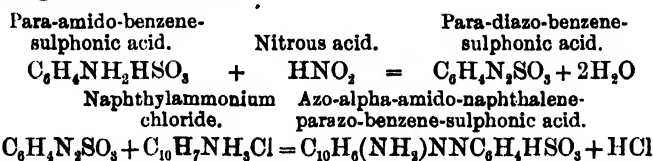
#### ANALYTICAL PROCESS :—

100 c.c. of the water is placed in one of the colour-comparison cylinders, the measuring vessel and cylinder having previously been rinsed with the water to be tested. By means of a pipette, one c.c. each of the solutions of sulphanilic acid, dilute hydrochloric acid and naphthylammonium chloride is dropped into the water in the order named. It is convenient to have three pipettes for this test, and to use them for no other purpose. In any case, the pipette must be rinsed out thoroughly with nitrite-free water each time before using, as nitrites in quantity sufficient to give a distinct reaction may be taken up from the air.

One c.c. of the standard nitrite solution is placed in another clean cylinder, made up with nitrite-free water to 100 c.c. and treated with the reagents as above.

In the presence of nitrites a pink colour is produced, which in dilute solutions may require half an hour for complete development. At the end of this time the two solutions are compared, the colours equalised by diluting the darker, and the calculation made as explained under the estimation of nitrates.

The following are the reactions :—



The last-named body gives the colour to the liquid.

This extract will show that the book is really well written, and will be found very useful to those whose libraries are not already glutted with such literature.



**COMMERCIAL ORGANIC ANALYSIS : A TREATISE ON THE PROPERTIES, PROXIMATE ANALYTICAL EXAMINATION, AND MODES OF ASSAYING THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, ETC. ; WITH CONCISE METHODS FOR THE DETECTION AND DETERMINATION OF THEIR IMPURITIES, ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION.** By ALFRED H. ALLEN, F.I.C., F.C.S. Second edition, revised and enlarged. Volume III., Part I. London : J. and A. Churchill, New Burlington Street.

THE new volume of Mr. Allen's work, although waited for by most of the profession with considerable impatience, amply justifies the care bestowed on it by the author, and simply goes to prove that what is done deliberately is generally done well. The volume now before us is devoted to the consideration of the acid derivatives of the phenols, aromatic acids, tannins, dyes and colouring matters. To attempt anything like an exhaustive criticism of such a work within the space available in our columns would be to do justice neither to the book nor to our readers. No doubt by this time most of them have already added the volume to their libraries, and all we can say is that, if any have not yet done so, then the sooner they get it the better, because it is simply an unrivalled compilation of all the most recent matter that has appeared on the subject on which it treats. The author is nothing if not having a shot at somebody, and he is especially in his element when he can get at the pharmacopœia compilers. In this volume he has two capital chances over zinc sulphocarbolate and chrysophanic acid respectively. The chapter on tannins is very complete, many excellent tables of reactions, etc., being given, but the great bulk of the book is occupied by the dyes. The analytical instructions and tables for the recognition of the dye that has been used on any fabric, etc., extend over fifty pages, and no one can look at this part of the work without being forcibly struck with the enormous advance in analytical chemistry that has taken place within the present generation, and the rapidly approaching impossibility of any man saying, "I know chemistry." As years roll on chemists are driven to specialise and to devote themselves to some particular branch of analysis, and we venture to predict that the old general analytical chemist, who took up any analysis with a light heart, will soon become an extinct animal. If anything could work to help a man to be a sort of Admirable Crichton in analysis, it is the production of such books as this. Mr. Allen is to be congratulated on the continued successful progress of his heavy undertaking. From the advance in all organic work he will no sooner have issued Vol. III., Part 2, than he will have to start again on the revise of Vol. I. We fear that, to an author of such books, life must become at last something very nearly similar to the existence experienced by Mr. Mantalini of well-known celebrity for the terse way in which he expressed his feelings on the subject.

#### PRIZE OFFERED FOR A PROCESS OF BUTTER ANALYSIS.

THE Royal Society of Science in Denmark has offered a prize of Kr. 600 for a chemical investigation as to the fatty acids present in butter-fat, each acid to be isolated and sufficiently identified. The relative amount of the different fatty acids, of which the investigation is expected to give information, should be given with the methods employed, as far as they are new or otherwise of interest, and especially is wanted the proportion between oleic acid and palmetic acid with its higher homologues.

Papers, which may be written in Danish, Swedish, English, German, French, or Latin, are to bear no name but a motto, and a sealed envelope with the same motto, enclosing the name, position, and address of the author, must be sent with the paper, which should be sent before the 31st of October. 1890, to Dr. H. G. Zeuthen, Secretary of the Society.

# THE ANALYST.

NOVEMBER, 1889.

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## ON THE ESTIMATION OF SULPHUR IN PYRITES.

By G. LUNGE.\*

It is a well-known fact that the estimation of sulphuric acid as barium sulphate, is not quite accurate when the solution contains iron salts. Although the precipitate is always distinctly coloured by iron, the results are, however, slightly too low. The reason of this peculiar fact has been completely cleared up by the investigation of Jannasch and Richards; it is caused by the formation of an insoluble barium—iron sulphate. These analysts, therefore, condemn in their paper my process for the estimation of sulphur in pyrites as being inaccurate, but they do not mention that this can only refer to an old process of mine, published in my work on the soda industry, as already in 1881 I advised to first precipitate the iron with ammonia. I now hear that Jannasch finds this to be a perfectly reliable method. Looking at the immense importance of the process (every year perhaps a million tons of the article are sold on analytical certificates), I had already commenced a thorough investigation, so as to make everything perfectly clear. Let us first see, however, how matters stood before Jannasch's and Richards' investigation.

In my work on soda manufacturing, I have preferred to recommend the treatment of the pyrites with aqua regia, instead of the fusion with nitrate and carbonate of soda.

\* *Zeitschr. f. angew. Chemie*, No. 17, 89.

Fresenius, who made his assistants perform a number of analyses, however, showed the dry process to give better results, on account of the complete isolation of the iron. One of his assistants got even 1 per cent. of sulphur too low, which was attributed to the solvent action of the ferric chloride on the barium sulphate.

Now I found in 1881, first, that the presence of iron, as ferric chloride, renders the precipitation with barium chloride somewhat inaccurate, as the barium sulphate is always ferruginous, and can only be freed from iron by using large quantities of hydrochloric acid, which causes a loss of about 5 per cent. of barium sulphate. In two analyses the percentage of sulphur was found to be from 46.7 to 47.32 per cent.; average 46.98 per cent. I further proved that perfectly concordant and accurate results may be obtained by precipitating the iron with the smallest possible amount of ammonia, and washing the precipitate on a filter with boiling water. In all my experiments I tested for sulphuric acid in the ferric hydrate, by fusing with soda, and dissolving the mass in water, etc., but I have never found a trace of it, so it is a needless operation.

Then I showed that the second method gives a little more sulphur than the first, but after all, only about  $\pm$  .18 per cent. How they managed to get as much as 1 per cent. difference in Fresenius' laboratory, I think I can explain by their pyrites containing traces of galena, heavy spar, or even gypsum.

In some experiments by Jannasch and Richards, there could be no question of galena or heavy spar, but, as they observed, a prolonged ignition of the precipitate may cause volatilisation of some of the sulphate, and any increase in weight through presence of iron be more than counteracted through this loss. The problem to find a reliable process for sulphur estimation by a wet process, was sufficiently solved by my labours. The process has been generally introduced in Germany and England, and is the only accepted process in the German soda trade, and the many complaints, of analysts differing in their results (by using the older process), have gradually died out. I now wish to show that Jannasch's and Richards' objections only relate to my first published method. They describe twenty-five different experiments, which all again prove the already known fact that in presence of iron the estimation of sulphur as barium sulphate is incorrect. Their last experiment also *qualitatively* shows the formerly not known cause of this error, viz., the formation of an insoluble barium-iron sulphate, which, on ignition, slowly but gradually loses the part of the sulphuric anhydride which may be supposed to be in combination with the iron. They say: The experiment (heating the precipitate at a bright-red heat) can be continued for half an hour without getting rid of the fumes of sulphuric anhydride, and the precipitate is constantly increasing in colour. Whilst they got from 10 c.c. of their normal acid 1.1608 gram. barium sulphate in absence of iron, when this was added they got an average of only 1.117, or about 4 per cent. too little. These remarkably large differences, which far exceed those got by Fresenius, no doubt were caused by the unusual and continued ignition. However, their experiments once more conclusively show that the estimation of the sulphur in presence of iron is not reliable, and regularly gives results too low, although the loss must vary according to circumstances. But this does not occur when the iron is first removed by means of ammonia, which process is, however, not mentioned in any of their twenty-five experiments. True, they casually mention that the previous precipitation of the

iron by ammonia is inadmissible, since even after a double precipitation the precipitate still retains .5 per cent of sulphuric acid (as basic ferric sulphate). They do not, however, seem to have made any accurate experiments themselves. We will also presently see that it really depends on how the precipitation is performed, and that if sufficient care is not taken, even a far greater quantity than .5 per cent. will be retained by the precipitate. But, as already mentioned, I took care not to commit any errors, and have convinced myself of the absolute absence of sulphuric acid from the precipitate. Now all this ought to be a sufficient answer to those who think my process inaccurate, but the matter being of such vast analytical importance, I resolved to again investigate the matter from beginning to end. As, however, my many professional duties prevented me from doing the analyses myself, I have had them performed by two gentlemen in whose abilities I place the greatest confidence, and who have investigated the matter quite independently of each other.

Ch. Barbezat prepared (as I did in 1881) a solution which represented an iron pyritis, viz., contained 2 molecules of sulphuric acid for 1 atom of iron. The solution was not only pipetted off, but also weighed. The liquids were precipitated by ammonia, the ferric hydrate washed with boiling water, and, after drying, fused on the blow-pipe with soda. After dissolving in water and filtering, hydrochloric acid and barium chloride was added, and the fluid allowed to stand a long time. Now a remarkable fact was disclosed. In his first two experiments, Barbezat brought the iron sulphate solution to boiling heat, added ammonia till it had a faint smell, boiled until smell had disappeared, and then collected and washed on to a filter, until the filtrate measured nearly 700 c.c. The dried precipitate gave, after fusion with soda, a very distinct reaction for sulphuric acid, which, when weighed, amounted to 3.6 per cent. of the total, or a still larger error than got by Jannasch and Richards, who only found .5 per cent.

Now, in my description of the process, I have particularly laid stress on using a moderate *excess* of ammonia. I said: "The moderate hot fluid is mixed with a not too large excess of ammonia, filtered off after about ten minutes, and washed on the filter with boiling water until the filtrate gives no longer a cloud with barium chloride, even after some time." His attention being called to this, Barbezat repeated the experiments, and now found in three cases *not a trace*, and in another case only the merest sign of sulphuric acid, and this trace was most likely caused by absorption of sulphurous vapour during the fusion.

The experiments conducted by Anast Obregia are more to the point. He worked with iron pyritis itself, which he had obtained from Spain, and which was free from copper, lead, and other sulphides. From the finely agated sample, 1 gramme was taken for analysis. Experiments were made (a) with my old process, without separation of iron; (b) with my modified process of 1881; (c) with Fresenius' process, the fusion with soda and nitre. (a) and (b) were heated exactly according to my directions with aqua regia, consisting of one part of fuming hydrochloric acid and three parts of nitric acid of 1.4 sp. gr., both, of course, free from sulphate. The evaporation on the water-bath takes about fifteen minutes, and no free sulphur separates. When dry, the mass is treated twice with excess of hydrochloric acid, and again evaporated. 100 c.c.

of water and four drops of hydrochloric acid are then added, and the liquid filtered from any gangue.

Three experiments (a) were performed. The boiling fluid was directly mixed with barium chloride, and after standing for about forty-five minutes, the precipitate was first washed by decantation, and finally washed on the filter with boiling water. The washings did not get turbid on standing, and the ignited precipitates were all crimson-red.

Five experiments (b) were made. The filtrate, measuring about 100 c.c., was slightly warmed and mixed with ammonia, until it acquired a strong colour. After ten minutes the precipitate was washed on a filter with boiling water, until the filtrate gave not the slightest cloud with barium chloride.

Now, Obregia exactly carried out my plan: to choose a rather large funnel, which is so made that the filter exactly fits it, and the filtrate constantly fills its stem. The water must be really boiling, and squirted into the centre of the ferric hydrate so as to get a thin paste, and prevent formation of channels. Working in this way, both ferric and aluminic hydrates may be conveniently washed on a filter, without the troublesome decantation. Obregia found the washing to last from three-quarters to one and a-half hour, according to the quality of the filter-paper. The total volume of the filtrate seldom exceeded 250 c.c., so that there was generally no need for concentration before estimating the sulphuric acid.

The ferric precipitates were now each time dried and fused in a platinum crucible with perfectly pure soda. The fusion was carried out by placing the crucible in a perforated sheet of asbestos, and heating with a Bunsen burner. This simple arrangement prevents the access of sulphury vapours, and renders unnecessary the use of a Berzelius lamp, as used in Jannasch's and Richards' experiments. The mass was now exhausted with water and tested as usual for a sulphate. Even after standing for twelve hours, not a trace of it could be detected. If, therefore, one only works according to my directions, the ferric oxide will be perfectly free from sulphur. The precipitation of the iron free liquid was done with barium chloride as usual. The barium sulphate, after being ignited, was always perfectly white.

Three experiments (c) were carried out. The ore was fused with ten times its weight of a mixture of two parts of soda and one part of nitre, in a platinum crucible placed in asbestos, with all the precautions recommended by Fresenius. It must, however, be observed, that this method requires more manipulating skill, and takes at least double the time of the aqua regia process, and that it also quickly spoils the crucibles. The following percentages of sulphur were obtained:—

| A                      | B                        | C                      |
|------------------------|--------------------------|------------------------|
| Lunge's old<br>method. | Lunge's method,<br>1881. | Fresenius's<br>method. |
| 52.38                  | 52.70                    | 52.46                  |
| 52.38                  | 52.14                    | 52.49                  |
| 51.94                  | 52.22                    | 52.31                  |
|                        | 52.26                    |                        |
|                        | 52.39                    |                        |
| Average                | 52.23                    | 52.42                  |

From these results I now can, with the greatest of certainty, draw the following conclusions:—

1. My process of 1881, viz., the acid treatment of the pyrites, and removal of the iron by ammonia, before precipitating the sulphate, gives completely concordant results with the fusion process of Fresenius. Even when the first experiment (B) is rejected, the average still comes to 52·32 per cent., therefore differing only ·10 per cent. from Fresenius' figures, who, in his own laboratory, with his own process, got far greater differences, viz., from 43·74–44·04 per cent. so ·3 per cent.

2. By these proved facts, also by the direct testing of the ferric precipitates, it is shown that when working properly, no sulphuric acid is retained. In this view I am supported by Barbezat and Obregia.

3. The former opinion of Jannasch and Richards, that my process ought to be rejected from a purely scientific point of view, does not relate to my process of 1881. This process is, at least, quite as accurate as the one of Fresenius, but has, besides, the advantage of being performed in much less time (not without advantage to works-chemists), and many analyses can be carried on at once. It further saves the wear and tear of the platinum crucibles; and last, not least, it is applicable in cases when the ore contains heavy spar, which renders Fresenius' process unreliable. Therefore my process of 1881, on account of its easy execution and reliability, deserves the preference over others, in the estimation of sulphur in pyrites.

4. My older process, which does not provide for removal of the iron, gives, as I found in 1881, results which are too low, but only by ·17 or ·19 per cent. In 1889 I found it to be ·18 per cent. Jannasch and Richards got far greater differences, but this is most likely caused by their extraordinary system of prolonged and intense ignition, such as nobody would think of doing. The process may, therefore, be trusted to yield results quite accurate enough for technical purposes, but in more important cases of buying and selling large quantities, my new process is to be preferred.

## ANALYSIS OF WATER FOR DOMESTIC PURPOSES.\*

By FERD. FISCHER.†

THERE is scarcely a branch of analytical chemistry where exist so many different views as in water analysis. Since analyses of potable waters are mostly done by professional analysts, instead of medical men, the chemical work has certainly become more exact; but the conclusions drawn from it are still, in many cases, incorrect, and do not rest upon sound foundation. Since Koch's discovery of the cholera baccillus, many medical men have taken to the bacteriological method, which in itself is very praiseworthy, if not too exaggerated conclusions are at once drawn. Plagge and Proskauer are of opinion that the chemical composition of a water goes for nothing; all they require

\* Slightly abridged from the original.

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being freedom from infecting matter, but they do also confess that this matter can but seldom be proved by the bacteriological research. Other chemists, although not objecting to a chemical analysis, will not form any opinion without a bacteriological investigation.

A normal water, according to Koch, is such a one which contains in one c.c., less than 300 germs. Plagge and Proskauer, however, do not allow more than 50 or 150 at the most, which latter number is the one fixed by the Swiss Society of Analytical Chemists. A. Pfeiffer, however, condemns a water, when it gives the figures 1000; If the counting of germs really sufficed to judge a water by, a chemical analysis would be superfluous, and any intelligent person might readily learn water analysis by attending a fortnight's course of cramming in some hygienic institution.

On the spread of infectious diseases by means of drinking water, the medical profession has not yet quite agreed. Whilst Koch and his adherents have found the cholera bacillus in an Indian tank, and have proved the spread of cholera through the use of that water, their statement is still doubted by Pettenkofer and his school. According to Emmerich and Trillish, a sure detection of the typhoid bacilli in water is as yet impossible, and it is not at all proved that the cholera vibrioni, noticed by Koch, are really the actual source of cholera in human beings. C. Cramer, in his paper on the water supply of Zürich, is of opinion that it is as yet impossible to find the typhoid germ when it has left the human body, and it must also be considered the bacilli often completely disappear. The Zürich commission appointed to investigate the matter, unanimously rejected the bacteriological process.

Under such circumstances, it sounds strange to demand a water to be especially free from infecting matter when this cannot be proved. But even if this were possible, it is certainly as yet quite undecided, whether the bacilli generally occurring in water are not quite as harmless as the many millions which a person swallows during a day, in the shape of sour milk, cheese, etc. The value of the germ-counting process becomes still more doubtful, as it is influenced by numerous circumstances. Wollffhügel and Riedel pretend that even the motion of the water is of influence on the germ number, and that it is also influenced by the temperature. One sample, when freshly taken, stood the test all right; but after it had been kept for a short time in a room it was proved to be dangerous to life.

It must also be considered, that some pathogenic bacteria in water are stunted in their growth by the presence of masses of other unpretending bacteria. According to Piefke the purification of water in filters is actually caused by bacteria. The presence of the harmless bacteria is, therefore, even a good sign, and shows the fallacy of the germ-counting process. In judging a water for domestic purposes, one has to decide whether or not it is free from human or animal excrements. It is, however, rare to actually find such matter, as they very rapidly decompose into other bodies of doubtful chemical composition, and under the influence of oxygen soon yield carbonic acid, ammonia and nitrous or nitric acids. The decomposition goes quickest in rapid waters, and more quickly still in porous soils. If an analyst has now to give an opinion on a spring water he must get information about the nature of the soil. Most soils will retain phosphates, potash, ammonia and nitrogenous bodies, whilst chlorides and nitrates, also sulphates, are kept in solution. Chlorides in particular point strongly to the presence of urine. If the soil

has lost its absorbing power and the oxygen supply is insufficient, the water will show nitrites, ammonia, and decomposing organic matter. Therefore, unless the nature of the soil is known, no safe conclusions can be drawn from the components of a sample of water.

To judge of the quality of a water intended for domestic purposes one has to look, therefore, for such bodies as are connected with human or animal excrements, viz., decomposing organic matter, ammonia, nitrous acid, nitric acid, and chlorine. It is of little use to estimate anything else.

It has been proposed by Schulze, Almén, and also by Reichart, to fix certain standards or limits to be used by every analyst. I have already demonstrated that those limits were far too exacting, and, for instance, did not suit the town of Hanover. It will be seen from the table the numbers proposed by Tieman and Gärtner and the Swiss Society are very close, whilst the International Congress at Brussels proposed figures which cannot be accepted. The English Commission, 1868, attached most importance to the organic matters. The thoughtless application of these figures must give rise to the greatest confusion, but they are certainly not without any value at all, as when they exceed the limit, a water may be regarded as suspicious. Nobody has, however, a right to declare a water dangerous to health, or advise a well to be closed on the mere strength of a chemical, and less still a microscopical, analysis of a sample, unless the well and its surroundings have been thoroughly inspected.

TABLE SHOWING THE LIMITS OF IMPURITY AS PROPOSED BY VARIOUS AUTHORITIES

(Translated into grains per gallon).

| Grains per Gallon.                              | Reichart,<br>1872. | Fischer,<br>1873,<br>for Hanover. | Tieman,<br>1874. | English<br>Commission,<br>1874. | Brussels<br>Congress,<br>1885. | Swiss Society,<br>1888. | Tieman and<br>Gärtner,<br>1889. |
|---|--------------------|-----------------------------------|------------------|---------------------------------|--------------------------------|-------------------------|---------------------------------|
| Organic matter<br>as $K_2M_2O_7$ ,<br>including | ·14—·70            | ·56—1·02                          | 4·2—7·0          | —                               | ·70                            | ·70                     | ·42—·70                         |
| Org. Carbon                                     | —                  | —                                 | —                | 1·40                            | —                              | —                       | ·35                             |
| „ Nitro-<br>gen.. ..                            | —                  | —                                 | —                | ·021                            | —                              | —                       | —                               |
| Albumenoid                                      |                    |                                   |                  |                                 |                                |                         |                                 |
| Ammonia ..                                      | —                  | —                                 | —                | —                               | ·007                           | ·0035                   | ·014                            |
| Ammonia ..                                      | —                  | 0                                 | 0                | —                               | ·035                           | ·0014                   | 0                               |
| Nitrous Acid..                                  | —                  | 0                                 | 0                | —                               | —                              | 0                       | 0                               |
| Nitric Acid ..                                  | ·28                | 1·89                              | 3·5—10·5         | —                               | ·14                            | 1·40                    | ·35—1·05                        |
| Chlorine ..                                     | ·14—·56            | 2·42                              | 1·40—2·10        | —                               | ·56                            | 1·40                    | 1·40—2·10                       |
| Sulphuric Anhy-<br>dride ..                     | ·14—4·41           | 5·60                              | 5·60—7·0         | —                               | 4·20                           | —                       | 5·60—7·00                       |
| Residue ..                                      | 7—35               | —                                 | 35·0             | —                               | 35·0                           | 35·0                    | 35·0                            |
| Hardness ..                                     | 12·6               | 11·9—14·0                         | 12·6—14·0        | —                               | 16·0                           | —                       | 12·6—14·0                       |



# ESTIMATION OF EXTRACTIVE AND SPECIFIC GRAVITIES OF OFFICIAL TINCTURES.

By J. SPILSBURY, F.C.S., *Pharm. Ch.*

THE following summary of averages is based on estimations extending over a period of ten years. The tinctures from which the samples were taken having been manufactured, under my personal supervision, from fine specimens of crude drugs (not specially selected samples) and strictly in conformity with the formulæ of the British Pharmacopœia.

The evaporations were conducted in thin porcelain basins of about 2½ ins. in diameter, with the exception of some rectified tinctures which had a tendency to creep over the sides, in which cases glass beakers of about 2 oz. capacity were substituted. The respective residues were exposed on the water-bath to a temperature of 212° Fah. and weighed at the expiration of two hours :

|                              | Extractive<br>from 10 c.c.<br>expressed<br>in grammes. | Specific<br>Gravity<br>at<br>60° Fah. |                                    | Extractive<br>from 10 c.c.<br>expressed<br>in grammes. | Specific<br>Gravity<br>at<br>60° Fah. |
|------------------------------|--|---------------------------------------|------------------------------------|--|---------------------------------------|
| Tincture of Aconite ..       | ·231   | ·855                                  | Tincture of Jaborandi ..           | ·232   | ·928                                  |
| „ Aloes ..                   | ·588   | ·961                                  | „ Jalap ..                         | ·355   | ·940                                  |
| „ Arnica ..                  | ·029   | ·842                                  | „ Rhatany ..                       | ·314   | ·937                                  |
| „ Asafetida ..               | ·643   | ·865                                  | „ Larch ..                         | ·128   | ·846                                  |
| „ Orange ..                  | ·335   | ·935                                  | „ Lobelia ..                       | ·301   | ·939                                  |
| „ Orange from<br>fresh fruit | ·256   | ·894                                  | „ Lobelia<br>(Ethereal)            | ·105   | ·824                                  |
| „ Belladonna ..              | ·083   | ·926                                  | „ Hop ..                           | ·267   | ·930                                  |
| „ Benzoin ..                 | 1·526  | ·889                                  | „ Myrrh ..                         | ·366   | ·849                                  |
| „ Buchu ..                   | ·179   | ·939                                  | „ Nux Vomica ..                    | ·122   | ·888                                  |
| „ Calumba ..                 | ·094   | ·928                                  | „ Opium<br>(simple)                | ·416   | ·936                                  |
| „ Indian Hemp                | ·430   | ·846                                  | „ Pyrethrum                        | ·153   | ·860                                  |
| „ Capsicum ..                | ·080   | ·843                                  | „ Quassia ..                       | ·002   | ·921                                  |
| „ Cardamoms                  | ·567   | ·944                                  | „ Quinine ..                       | ·532   | ·939                                  |
| „ Cascarilla ..              | ·100   | ·932                                  | „ Rhubarb ..                       | ·538   | ·955                                  |
| „ Catechu ..                 | 1·068  | ·961                                  | „ Savin ..                         | ·235   | ·933                                  |
| „ Chiretta ..                | ·118   | ·927                                  | „ Squill ..                        | ·878   | ·953                                  |
| „ Cimicifuga                 | ·208   | ·929                                  | „ Senega ..                        | ·318   | ·931                                  |
| „ Cinchona ..                | ·470   | ·939                                  | „ Seuna ..                         | ·835   | ·893                                  |
| „ Cinchona<br>(compound)     | ·439   | ·937                                  | „ Serpentry                        | ·087   | ·911                                  |
| „ Cinnamon                   | ·140   | ·928                                  | „ Stramonium                       | ·045   | ·939                                  |
| „ Colchicum                  | ·100   | ·926                                  | „ Sumbul ..                        | ·365   | ·931                                  |
| „ Hemlock ..                 | ·243   | ·942                                  | „ Tolu ..                          | 1·223  | ·880                                  |
| „ Cubebs ..                  | ·118   | ·846                                  | „ Valerian ..                      | ·208   | ·928                                  |
| „ Digitalis ..               | ·407   | ·939                                  | „ Valerian<br>(Ammon-<br>iated) .. | ·237   | ·907                                  |
| „ Ergot ..                   | ·200   | ·932                                  | „ Veratrium                        | ·189   | ·847                                  |
| „ Galls ..                   | 1 215  | ·978                                  | „ Ginger<br>(strong)               | ·197   | ·847                                  |
| „ Gelseminum                 | ·118   | ·929                                  |                                    |  |                                       |
| „ Gentian ..                 | ·398   | ·939                                  |                                    |  |                                       |
| „ Guaiacum                   | 1·392  | ·939                                  |                                    |  |                                       |
| „ Henbane ..                 | ·299   | ·930                                  |                                    |  |                                       |

The inference deduced in obtaining the foregoing results indicates that tinctures manufactured under similar conditions should not vary from the average amount of extractive in the proportion of more than ·01 gramme for every ·5 gramme yielded, 10 c.c. of Tincture being used for the evaporation.

## MILK ANALYSIS.

BY DR. BENNETT F. DAVENPORT.\*

IN the discussion of the relative merits of the different methods of milk analysis which was published in the June number of THE ANALYST, the many advantages of a simple modification of Wanklyn's method does not, I think, receive its due consideration. This modification, which I have adopted, I have already published in my Annual Report as Milk Inspector for the City of Boston, Mass., 1885, and as Analyst to the Massachusetts State Board of Health in their Annual Report for 1886, page 138. As being now the method generally followed by most of the official milk analysts in New England, a simple description of it may be of interest to others.

The 5 grms. of milk are weighed off in a large flat-bottom platinum capsule of full  $2\frac{1}{2}$  inches diameter on the bottom, and about 3 inches across the top. The  $\frac{1}{2}$ -inch high side turns up from the bottom, not with a sharp angle, but slight rounding, this being about the curve with which the milk runs up the rim of the capsule drawn by capillarity. The milk in drying down does not thus form any thicker deposit at the angle of the side than elsewhere upon the about 5 square inches of bottom surface of the capsule. This relatively large amount of surface, one square inch to each gm. of sample taken, causes each inch to be covered with only a little over a single grain of dried milk solids. The deposit is therefore so very thin as to be readily exhausted of its fat in its subsequent treatment with boiling petroleum naphtha. When using such small dishes as were originally proposed by Wanklyn, the residue would be so thick, that is about three times, as would naturally render any such rapid method of extraction as I employ impossible, as the English analysts have learned. Each capsule has its serial number engraved upon it, and they are made to weigh a little over 25 grms. each, that the bottoms may be stiff enough to remain perfectly flat—a matter of very great importance. They are also made to differ from each other only in the second and third places of decimals, so that only those weights have to be changed in many weighings, which is a matter of no little saving of labour where many score of weighings are to be made each day. A table of their weights is kept within the case of the scales. These capsules, containing their samples, are placed upon a constant-level closed-top water-bath, of the peculiar construction described on page 269 of the *Journal of Analytical Chemistry*. This will hold twenty-five capsules at a time. Here, being surrounded by atmosphere not already nearly saturated with moisture, as would be the case if they were upon a water-bath with openings on its top, they quickly evaporate to apparent dryness. They are then transferred for their final drying to a constant weight to one of Weisnegg's large porcelain-lined air-baths, regulated to the constant temperature of  $105^{\circ}$  C. Here they are dried in about half an hour, when they are cooled in a desiccator and each weighed immediately upon being taken out, to guard against their rapid gain in weight from exposure to the air. Replaced upon the closed-top water-bath, the capsule is filled from a wash bottle with petroleum naphtha, of the quality of the benzine of the U. S. Pharmacopœia, revision of 1880. This, unlike ether, will dissolve out neither milk-sugar nor lactic acid from the dried milk-solid residue. Moreover, one gallon of it costs but as much as one pint of ether would, which is a matter of some little con-

\* *Journal of Analytical Chemistry*.

sequence to one like me, who has had to use about 100 gallons of it in milk analyses during the past five years.

The naphtha in the capsule, after being allowed to boil down about one-half, is decanted off against a rod into a basin to guard against the remote possibility of some flakes of milk residue being poured off with it. Replaced upon the bath, the capsule is refilled with naphtha. This boiling up and decanting off is repeated three to four times, when after the last one the outside of the capsule is washed off with naphtha played upon it from the wash-bottle, to prevent any residue of fat being left there. The capsule, then finally replaced upon the bath to dry off the naphtha, is then cooled and weighed as before, the butter being rather determined from the loss of weight in the solids than by the weight of the evaporated washings.

The ash is made by ignition of the capsule over a one-inch wide Bunsen lamp, which thus gives so wide a flame as not to require a heating to a high temperature at one point, and thus a possible loss by the volatilisation of the potassium chloride. The milk-sugar I determine by the use of a Soleil-Ventzke saccharimeter, in the same manner as has now been several times described in the journals by Drs. Wiley, Vieth, and others. The other ingredients which reduce copper in Fehling's solution, are not thus reckoned as sugar, by which the apparent amount of albuminoids present, which are obtained by difference, would be diminished.

The peculiarities of my modification is then the use of an evaporating capsule of such a very large relative area as will leave the residue thin enough to be readily exhausted by the boiling naphtha. Thus a diameter of  $2\frac{1}{2}$  inches in the capsule will do for 5 grms. of better than average quality of milk, with a surety that there will not be as much as one-tenth of 1 per cent. of fat left as a maximum error. And surely this is fine enough for all commercial work, and it is much to be doubted if much which affects to be more accurate by a decimal than this is really so. The method, as involving no transfer of substance, cannot well be made more simple for the determination of total solids, fat and ash. When the average life of such an evaporating capsule under reasonable usage is considered, it cannot well be cheapened, although the outlay for a kilo. of platinum for forty capsules like mine does, it is true, involve an original expense of nearly 400 dollars. The shape of my capsules makes possible completeness of extraction with the solvent used, and the construction of the closed water-bath hastens the process in no small degree.

#### ON SOME RESULTS OF ANALYSES OF OLIVE OIL FROM DIFFERENT SOURCES.

By LEONARD ARCHBUTT.\*

THE examination at various times during the past seven or eight years of samples taken from large bulks of olive oil intended for lubricating has afforded an opportunity of making a comparison of the oil from several different sources; but as, unfortunately, only a fraction of the samples have been labelled with the port of shipment, the number available for purposes of comparison is not so large as it might have been.

The results are arranged in the following table, and the following conclusions may be drawn from them :—

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\* *Journal of the Society of Chemical Industry.*

| Source of the Oils. | Total Number of Samples. | Number Examined for Adulteration as well as for Acidity. | Number found Genuine. | Per Cent. found Genuine. | Free Fatty Acid (=Oleic Acid). |         |          |
|---------------------|--------------------------|--|-----------------------|--------------------------|--------------------------------|---------|----------|
|                     |                          |  |                       |                          | Highest.                       | Lowest. | Average. |
| Seville .. ..       | 32                       | 32   | 31                    | 96·8                     | 10·0                           | 1·5     | 4·4      |
| Malaga .. ..        | 35                       | 35   | 27                    | 77·1                     | 25·1                           | 2·0     | 6·7      |
| Unknown .. ..       | 3                        | 3  | 2                     | 66·6                     | 5·6                            | 2·1     | 3·3      |
| Spain (total) ..    | 70                       | 70   | 60                    | 85·7                     | 25·1                           | 1·5     | 5·5      |
| Gallipoli .. ..     | 19                       | 18   | 17                    | 94·4                     | 16·9                           | ·9      | 7·3      |
| Gioja .. ..         | 12                       | 8  | 8                     | 100·0                    | 25·2                           | 4·1     | 10·9     |
| Monopoli .. ..      | 3                        | 3  | 3                     | 100·0                    | 8·6                            | 4·1     | 6·3      |
| Naples .. ..        | 2                        | 1  | 1                     | 100·0                    | 9·4                            | 9·2     | 9·3      |
| Italy (total) ..    | 36                       | 30   | 29                    | 96·7                     | 25·2                           | ·9      | 8·5      |
| Sicily (Messina)    | 28                       | 22   | 9                     | 40·9                     | 16·6                           | ·5      | 9·1      |
| Greece (Zante) ..   | 2                        | 2  | 2                     | 100·0                    | 8·7                            | 4·8     | 6·7      |
| Candia .. ..        | 12                       | 10   | 6                     | 60·0                     | 16·8                           | 5·5     | 9·5      |
| Levant .. ..        | 3                        | 3  | ..                    | ..                       | 13·5                           | 8·5     | 10·4     |

The Seville oils, both as regards their freedom from acidity, and the high percentage of genuine samples among them, prove to be superior to the famed Gallipoli oils. The acidity of some of the samples of Malaga oil was very high, but the average acidity was less than that of any of the Italian oils, except those from Monopoli, of which only three samples were examined. Among the Malaga oils there was a large percentage of adulterated samples. Taking the Spanish oils generally, although they appear from these results to be more liable than the Italian oils to be adulterated, yet, on the other hand, they are as a rule decidedly more neutral, which, as regards lubrication and burning, is a very important point.

Amongst the Italian oils those from Gioja are distinguished for their acidity. The small number of adulterated Italian oils is worthy of note.

My analyses of the oils from Sicily quite confirms their reputation for inferiority. They are very largely adulterated, and as a rule decidedly rancid.

A few single samples from sources not named in the table have also been examined. Thus, some oil from Mitylene proved to contain as much as 30 per cent. of free fatty acid. A sample labelled "Sfax Fine Olive Oil" gave the following results:—

|  |                     |
|--|---------------------|
| Sp. gr. at 60° F. .. .. .  | ·9169               |
| Free fatty acid (= oleic) .. .. .  | 13·5 per cent.      |
| Rise of temperature with sulphuric acid of 97 per cent. strength .. .. . | 43·5° C.            |
| Percentage of KOH required for saponification .. .. .                    | 19·38 per cent.     |
| Melting point of fatty acids by capillary tube }<br>method .. .. .       | 28° C. and 28·5° C. |

The Elaidin required 310 minutes to solidify at  $19^{\circ}$  C., and was dark lemon yellow and soft after standing 24 hours at  $19^{\circ}$  C.

The oil showed no unusual tendency to dry when tested side by side with olive oil of known purity.

By Renard's process no Arachis oil was found.

By the Miliu-Stock test no cotton oil was found.

The melting point of the fatty acids is quite abnormally high, and so also is the specific gravity, considering the large percentage of free fatty acid in the sample. No conclusions can be drawn, however, from the results yielded by this single sample. Another African oil, from Saffi (Morocco) gave quite normal results.

### DYNAMICAL THEORY OF ALBUMINOID AMMONIA.

By ROBERT B. WARDER.\*

THE following investigation was suggested by committee work of the American Association for the Advancement of Science, on water analysis. It is an attempt to apply well established principles of mass action to certain questions involved in the determination of albuminoid ammonia. The following points have been kept in view:

1. Can some probable correction be made for the error incurred by stopping the distillation while ammonia is still coming off?

2. What modification of the original method seems rational?

3. What insight can be gained into the nature of the chemical process?

The experimental basis of the following paper will be found in Mallet's report on the determination of organic matter in potable water,† with the addition of some details kindly communicated by Dr. Charles Smart.

#### I. *Distillation of Free Ammonia.*

In the distillation of albuminoid ammonia, two stages must be distinguished: first, oxidation of the nitrogenous body by the alkaline solution of permanganate; and, second, the separation of ammonia thus formed by distillation. It will be most convenient to begin with the discussion of this second process, which is essentially physical. As in any other case of fractional distillation, water and ammonia both pass from the fluid to the gaseous or vapour condition, in accordance with their respective tensions and mass.

Let  $x$  = volume of fluid in retort.

$y$  = weight of ammonia in retort.

$z$  = weight of ammonia in distillate.

Then  $\frac{y}{x}$  = concentration of fluid in retort,

$\frac{dy}{dx} = \frac{-dz}{dx}$  = concentration of any small portion of distillate.

The coefficient of volatility may be defined as the ratio of the concentration in any small portion of distillate to that of the fluid in retort. Designating this coefficient as  $k$ ,

$$\frac{dy}{dx} = k \cdot \frac{y}{x}. \quad (1)$$

\* *American Chemical Journal.*

† Report of the National Board of Health for 1882.

In the ordinary distillation of ammonia,  $k$  is found to be approximately constant, and it will be so regarded here. By integration,

$$\log_e y = k \cdot \log_e x + \text{constant};$$

using zero subscript to denote initial conditions,

$$\log_e y_0 = k \cdot \log_e x_0 + \text{constant},$$

$$\therefore \log_e \frac{y}{y_0} = k \cdot \log_e \frac{x}{x_0},$$

$$\text{or} \quad \log \frac{y}{y_0} = k \cdot \log \frac{x}{x_0} \quad (2)$$

a very useful formula for determining the coefficient of volatility and tracing the progress of distillation. Curve *A*, in the figure, represents  $y$  as that function of  $x$  defined by equation (2).

Wanklyn,\* who was the first to use and define the term coefficient of volatility, reports four experiments for its determination. One litre of dilute aqueous ammonia was distilled in each case until 50 cc. of distillate had been collected. As nearly one-half the ammonia taken was distilled with the first 5 per cent. of water (the concentration in the retort being gradually reduced at the same time), Wanklyn estimated  $k$  equal to "about thirteen or fourteen." The experimental data are given below with more precise values of  $k$ , as calculated by equation (2). In each case,  $x_0 = 1,000$ ,  $x = 950$ . The quantities of ammonia taken, and that found in the distillate, are expressed in milligrams. under  $y_0$  and  $z$  respectively; the difference (remaining in retort) under  $y$ :

| $y_0$ . | $z$ . | $y$ . | $k$ . |
|---------|-------|-------|-------|
| 1000    | 480   | 520   | 12.74 |
| 1       | .50   | .50   | 13.50 |
| .5      | .235  | .265  | 12.39 |
| .2      | .095  | .105  | 12.55 |

Mean = 12.8

This value may be rather too low, as no account is taken of a possible loss from imperfect condensation, a loss averaging 7.2 per cent. in Smart's experiments.

The same author observes also † that in the distillation of one-half litre of water, the ammonia found in the first measure of 50 c.c. is three-fourth of the whole quantity of ammonia obtained. By equation (2), assuming that any loss affects each part in the same proportion,

$$\log \frac{1}{4} = k \cdot \log \frac{1}{10},$$

$$\therefore k = 13.14.$$

Thirty experiments by Smart to determine the loss of ammonia by imperfect condensation are also available for the estimation of  $k$ , the successive measures of distillate having been nesslerised separately.‡ A single distillation affords several values, as each fraction determined may be compared with the whole quantity found in subsequent fractions. The values thus deduced vary from 10 to 16, with a few instances beyond these extremes. The variations in the values of  $k$  do not show any well marked relation to the whole quantity of ammonia present, to the amount of loss, nor to the

\* Phil. Mag. [4], 45, 132 (Feb. 1873).

† Wanklyn's *Water Analysis*, 6th and 7th editions, p. 41.

‡ Most of these data appear in the Report of the National Board of Health for 1882, pages 312-314.

rate of boiling. The experimental work was done wholly for another purpose, and probably with just such care as the conscientious analyst would ordinarily give. We may then assume 13 as a mean value for  $k$ , remembering that considerable allowance must be made for unexplained variations.

### II. Application of Formula to Estimation of Free Ammonia.

In the analytical process it is usual to distill three or four fractions, each nearly equal to one tenth of the original volume. For 100 parts of free ammonia present, when  $k = 13$ , theory would lead us to expect, in four successive fractions, the increments named below under  $\Delta z$ , with loss of 0.13; vertical lines in the figure,  $a, a, a$ , represent these increments geometrically. The ratio of each increment to the next is stated under  $r$ . The mean values of the ratios obtained in the experiments to determine loss of ammonia are given under  $r'$ :

| No. | $\Delta z$ . | $r$ . | $r'$ . |
|-----|--------------|-------|--------|
| 1   | 74.6         | 3.75  | 4.23   |
| 2   | 19.9         | 4.4   | 5.26   |
| 3   | 4.53         | 5.4   | 5.65   |
| 4   | .84          |       |        |

In the analyses of natural waters reported, considerable variation appears in the ratios of successive increments, but usually not more than might be expected from the observed variations in  $k$ . Analyses No. 18 and No. 54 are exceptional and happen to give identical results, the free ammonia being .015, .01, and .01 mgm. in the three fractions nesslerised, with ratios 1.5 and 1. In such cases there is a strong probability that some more complex body is gradually decomposed by simple boiling with sodium carbonate. Small ratios between the successive fractions of "free ammonia" may lead to suspicion of urea contamination, though of course due caution should be used in drawing such conclusions. The analyst will at least find it instructive to enter the ratios in his note-book, together with the separate results of nesslerising; this will appear more plainly in the following sections. The slowness of the chemical action usually retards the distillation of albuminoid ammonia, giving rise to much smaller ratios between successive fractions than those named above.

### III. Action of Mass in Formation of Albuminoid Ammonia.

We must now attempt to follow the chemical as well as the physical aspect of the process. In the former the reactions may be much involved, and various formulas may be required to represent the successive formation and destruction of different substances. Let us consider, as an ideal case, a single chemical reaction, involving one molecule each of three reacting bodies; the formation of ammonia taking place at each moment of distillation, in each cubic centimeter of the fluid, in proportion to the product of the quantities of the nitrogenous body, the potash, and the permanganate present therein.

Retaining the use of  $x$ ,  $y$ , and  $z$  as explained in section I, let

$u$  = weight of the nitrogenous body in the retort,

$v$  = weight of potash in the retort,

$w$  = weight of potassium permanganate in the retort,

$t$  = time, in minutes, from the beginning of the reaction,

$\alpha$  = coefficient of speed.

Assume also a uniform rate of distillation, in which

$b$  = volume distilled per minute,

$bc$  = volume of fluid in retort at the beginning of the action; whence

$$x = bc - bt,$$

and

$$dx = -b dt.$$

Then  $\frac{u}{x}$ ,  $\frac{v}{x}$ , and  $\frac{w}{x}$  = weights of the three active substances in each cubic centimeter of fluid in the retort,

$$-\frac{du}{dt} = b \frac{du}{dx} = \text{rate of change,}$$

and, by the law of mass action,

$$\begin{aligned} b \frac{du}{dx} &= \frac{u}{x} \cdot \frac{v}{x} \cdot \frac{w}{x} \\ \therefore \frac{du}{u} &= \frac{v w}{b} \cdot \frac{dx}{x^2}. \end{aligned} \quad (3)$$

The reagents are present in such large excess that  $v$  and  $w$  may be regarded as constants (unless the permanganate suffers from an unusual amount of pollution), and by integration,

$$\begin{aligned} \log_e u &= -\frac{v w}{b} \cdot \frac{1}{x} + \text{constant,} \\ \log_e u_0 &= -\frac{v w}{b} \cdot \frac{1}{x_0} + \text{constant,} \\ \therefore \log_e \frac{u}{u_0} &= -\frac{v w}{b} \cdot \frac{x_0 - x}{x_0 x}, \end{aligned}$$

which may be written

$$-\log \frac{u}{u_0} = \frac{v w}{b x_0 \log_e 10} \cdot \frac{x_0 - x}{x} = A \cdot \frac{x_0 - x}{x}. \quad (4)$$

This equation represents any one reaction of the kind specified during the concentration required in an ordinary estimation of albuminoid ammonia, but the mathematical expression must not be pressed too far. Thus, if we make  $x = 0$ , this not only implies that the contents of the retort are evaporated to dryness, but also that the reagents have gained infinite concentration, and therefore act with resistless force, effecting complete alteration of any remaining traces of the nitrogenous body. The form of the curve varies greatly with the value of  $A$ . Two examples are given in the figure. Curve  $B$  represents this equation when  $A = 1$ ; curve  $C$  when  $A = \frac{1}{10}$ . Since the quantity of ammonia present at any moment (both in retort and distillate) is proportional to the weight of the nitrogenous body transformed we may write

$$u_0 - u : u_0 :: (y + z) : (y + z)_\infty,$$

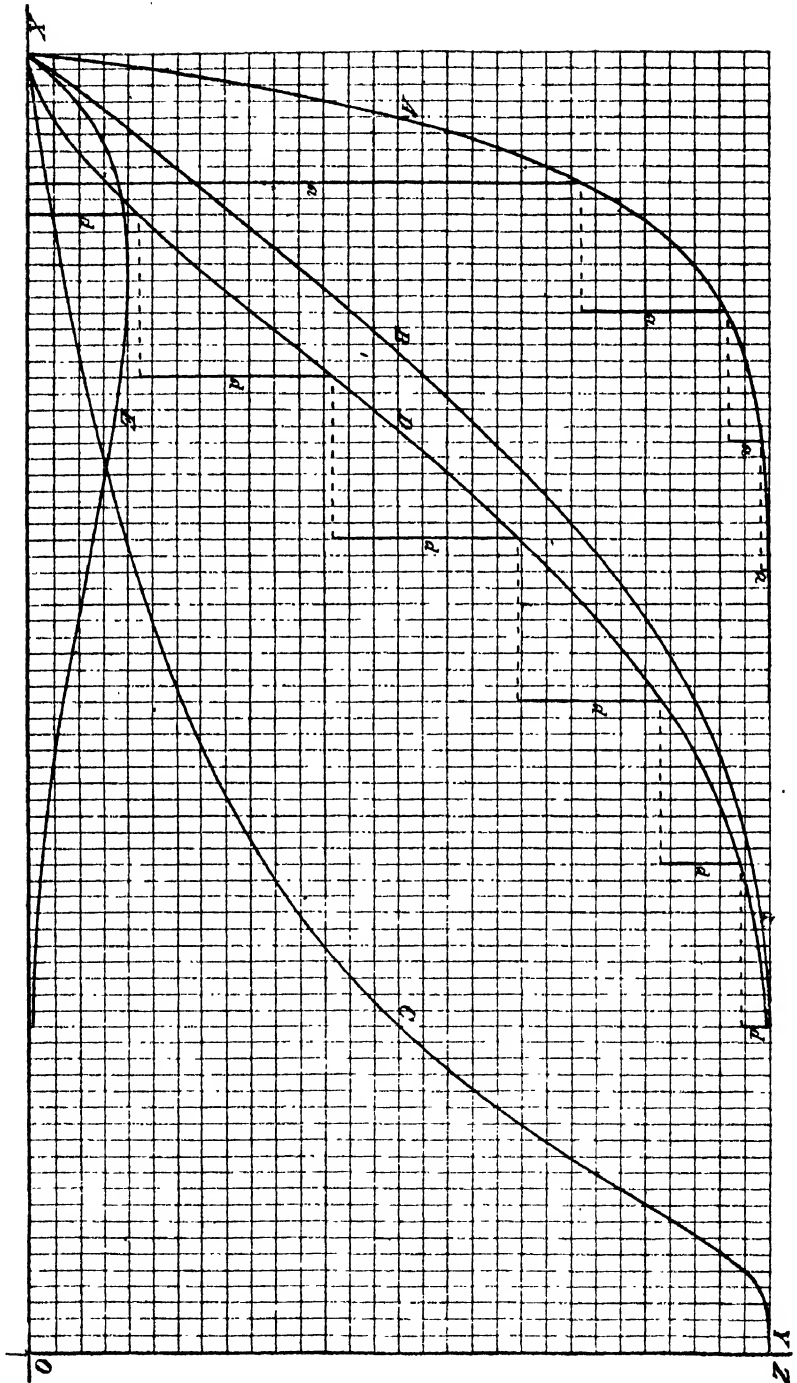
where subscript  $\infty$  is used to denote the ultimate value theoretically possible; or, in another form (since  $y_\infty = 0$ ),

$$\frac{u}{u_0} = \frac{z_\infty - (y + z)}{z_\infty}. \quad (5)$$

The curves  $B$  and  $C$  are so drawn that ordinates represent  $(y + z)$  as a function of  $x$ .

It will be seen at once that when  $A = 1$  the quantity of ammonia increases very rapidly during the first part of the distillation, but when  $A = 0.1$   $(y + z)$  increases but slowly until the fluid is considerably concentrated. Equation (4) suggests various modifications by which  $A$  may be altered at pleasure; for example, by increasing the quantity of permanganate used (represented by  $w$ ), or by distilling a less quantity ( $b$ ) each minute. Thus Smart noted several instances of increased action by slower boiling.





(To be continued.)

## EXPLANATION OF THE FIGURE.

A. Curve of distillation of free ammonia.  $a, a', a'', a'''$  Fractions, each  $\frac{1}{10}$  the original volume. B. Formation of albuminoid ammonia, eq. (7);  $A = 1$ . C. Formation of albuminoid ammonia, eq. (7);  $A = \frac{1}{10}$ . D. Ammonia is distillate, from curve B.  $d, d', d'', d'''$  Fractions, each  $\frac{1}{10}$  the original volume. E. Ammonia in retort, from curve B. Value of  $x$ , although positive, are measured towards the left, in order that time may be counted towards the right.

REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN  
ANALYTICAL PROCESSES.

THE SEPARATION OF COPPER FROM ANTIMONY. FINKENER. *Mitth. Königl. tech. Versuch*, 1889.—The separation is effected in two stages: first by the precipitation of the bulk of the copper, as cuprous iodide in an acid solution, and then by the removal of the remainder as sulphide in an ammoniacal solution. The author has established the following, which serve as a basis for the method:—(1.) Cuprous iodide carries down antimony even in the presence of tartaric acid from a nitric acid solution of the two metals, but does not do so if the antimony be first converted into a double salt of antimony pentafluoride and an alkaline fluoride by the addition of the latter. (2.) Free iodine in the presence of an alkaline fluoride converts antimony trifluoride into the pentafluoride. (3.) Sulphurous acid reduces antimony pentafluoride slowly in the presence of potassium iodide; the addition of hydrochloric acid hastens the reaction, but the presence of potassium fluoride almost completely inhibits it.

From this the following method is derived:—If the solution to be treated contain the antimony as a pentad compound, all that is necessary is to add an alkaline fluoride, then potassium iodide and sulphurous acid; heat gently, filter off the bulk of the copper as cuprous iodide, and wash with boiling water, made acid with sulphuric acid. In the event of the antimony being in the triad state the solution may be first treated with chlorine or bromine water, or oxidation may even be effected by the iodine liberated by the action of the cupric salt also present on the potassium iodide, provided time be allowed for it before the addition of sulphurous acid. The filtrate containing all the antimony and a little copper is oxidised by bromine water, and the metals precipitated together by sulphuretted hydrogen, the mixed sulphides dissolved in hydrochloric acid with the addition of potassium chlorate, ammonium tartrate added, and ammonia in excess; the resulting solution is heated on a water-bath and sulphuretted hydrogen added, until no further precipitation occurs. By thus minimising the quantity of ammonium sulphide present, re-solution of cupric sulphide is avoided. The filtrate containing only the antimony is acidulated with sulphuric acid and sulphuretted hydrogen passed through; the antimony is determined in the sulphide thus precipitated by heating it, together with its filter, with hydrochloric acid, and determining the sulphuretted hydrogen evolved by standard iodine solution. The author has established that antimony sulphide, precipitated in the presence of sufficient ammonium tartrate to convert all chlorine present into ammonium chloride, is of normal composition, and yields the theoretical quantity of sulphuretted hydrogen when heated with hydrochloric acid. The analytical results show the method to be reliable, if potassium or sodium fluoride in the proportion of about 1 grm. to 0.275 grm. of antimony be used, and the solution in which the first stage of the separation is effected be about 200 c.c.

W. H. D.

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ABNORMAL APPEARANCE OF CHOLERESTIN. J. B. NAGELVOORT. *Nederl. Eydscr. v. Pharmacie*, etc. October, 1889.—A sample of cod liver oil submitted to the author was tested in the usual way for phytosterin, and, indeed, the well-known needle-shaped crystals were obtained, apparently showing the presence of a vegetable fat. On applying the chemical tests, it was, however, proved to be cholerestin. On repeating the process,

the author succeeded in getting the proper crystals, but he fears their shape may be influenced by temperature, concentration of the liquid, and rate of evaporation, and, therefore, the mere appearance counts for nothing. The following reactions serve to recognise cholestin: Sulphuric acid gives a reddish-brown, turning to dirty green on adding a drop of water. A mixture of equal parts of chloroform and sulphuric acid gives a violet colour, changing to red and immediately discharged by a drop of water.

L. DE K.

ON THE ANALYSIS OF OLIVE OIL. RIOUL BRULLE (*Rev. Internal. des Falsification*, Oct. 15, 1889).—For the testing of olive oil, the author employs argentic nitrate in the presence of fuming nitric acid. The argentic nitrate decomposes violently, and produces metallic silver, with a coloration depending exactly on the nature of the oil employed. If we mix 10 c.c. of an oil with 0.5 c.c. of fuming nitric acid in a porcelain capsule, heat, and shake the mixture violently until a foam has been produced, we obtain different colours, according to the oils employed. We, however, take no notice of these, but go on with the process by adding 5 c.c. of a 25 per cent. solution of argentic nitrate in alcohol of 90°. Still applying heat, a moment arrives, at about 115° C, when the argentic nitrate decomposes, and deposits metallic silver. Having reached this point and continued to heat until the first flecks have just disappeared, we observe, on the one hand, the coloration of the slight oily stratum, which is easily seen by slightly inclining the capsule; and on the other hand, the metallic flecks glistening on the surface of the liquid. On saponifying the oils, and treating them by the same method, the colorations obtained are all different, as may be seen by the following table:—

| Oils.            | Colorations obtained. |                    |                |                |
|------------------|-----------------------|--------------------|----------------|----------------|
|                  | In the natural state. |                    | Saponified.    |                |
|                  | Oily strata.          | Flecks.            | Oily strata.   | Flecks.        |
| Olive            | Olive green           | Green              | Orange         | Brownish green |
| Cotton           | Green                 | Terra vert         | Raw sienna     | Cobalt violet  |
| Sesame           | Chrome green          | China blue         | Gold yellow    | " "            |
| Ground-nut       | Sap green             | Emerald green      | Persian lake   | Bright violet  |
| Poppy-seed       | Olive green           | Pale greenish blue | Gold ochre     | Blue           |
| Gold-of-pleasure | Persian lake          | Bright blue        | Deep chrome    | "              |
| Linseed          | Dragon's blood        | Emerald green      | Black          | Green [blue    |
| Colza            | Persian lake          | Brownish green     | Burnt carmine* | Ultramarine    |

\* After becoming cold, it forms a crystallization of blue-coloured needles on the surface.

The designations of the colours are those used in water-colour painting. In comparing the tint of any mixture of oils treated by this method with those given in the above table, a chemist will, after a little experience, be readily able to prove the presence of a seed oil in olive oil, as well as to detect adulterations as low as 5 per cent., and to name the foreign oil present in the sample.

M. S. A. M.

THE QUANTITATIVE ESTIMATION OF GALACTOSE. BY E. STEIGER (*Zeits. f. Anal. Chem.* 28, 444).—The author has prepared a table to calculate the quantity of galactose from the quantity of copper reduced; 60 c.c. of Fehling's solution diluted with an equal bulk of water is brought to boiling; 25 c.c. of the galactose solution, previously warmed, is added, and the mixture heated 3-4 minutes. The filtration was done by Soxhlet's Asbestos Filter (see Fresenius' "Quantitative Analysis," 6th edition, p. 596), and the copper oxide reduced in a current of hydrogen. The time—3-4 minutes—must be adhered to, Allibon (*Journ. f. Prakt. Chem.* 22, 72) having shown that by long heating (half an hour) a further précipitation of cuprous oxide occurs. The author's experiments show that from 3 to 7 minutes' heating, the results are the same.

The following table gives the mean of his results, obtained from two different samples of galactose, four estimations being usually made for each dilution:—

| Galactose. | Copper.    |
|------------|------------|
| 250 m.g.   | 434.5 m.g. |
| 237.5      | 411.8      |
| 225.0      | 393.6      |
| 212.5      | 375.0      |
| 200.0      | 354.2      |
| 187.5      | 335.0      |
| 175.0      | 316.4      |
| 162.5      | 297.6      |
| 150.0      | 277.5      |
| 137.5      | 254.0      |
| 125.0      | 232.7      |
| 112.5      | 211.1      |
| 100.0      | 188.7      |
| 87.5       | 165.4      |
| 75.0       | 142.4      |
| 62.5       | 120.2      |
| 50.0       | 94.8       |
| 37.5       | 73.1       |
| 25.0       | 49.9       |

H. D. R.

## REVIEWS.

COLOURED ANALYTICAL TABLES SHOWING THE BEHAVIOUR OF THE MORE COMMON METALS AND ACIDS TO THE ORDINARY REAGENTS, WITH SPECIAL REFERENCE TO THE COLOUR OF THE VARIOUS OXIDES, SALTS, PRECIPITATES, FLAMES, BORAX-BEADS, AND BLOWPIPE REACTIONS. A CLASS-BOOK FOR STUDENTS IN HOSPITALS, COLLEGES, AND SCHOOLS. BY H. WILSON HAKE, PH.D., F.I.C., F.C.S. London: G. Philip & Son, Fleet Street.

THIS book, with so voluminous a title, and a preface nearly filling two pages, is simply a set of the usual sort of imperfect analytical tables served up to the budding aspirants for ordinary medical primary examinations, and sufficiently full to get them through their arduous analytical labours in the (so-called) class of practical chemistry. It, however, differs from all other books with which we have met (except Dr. Simon's "Manual of Chemistry," published in 1885 and reviewed at the time in our columns), inasmuch as that, attached to each test there is a picture of a test tube showing a hand-painted representation of what the colour of the precipitate should be (supposing, of course, that the student works properly); and there are also similarly coloured representations of blowpipe beads, and charcoals, and of bunsen flames. What real advantage there will

be to the student other than enabling him to skulk his practical chemistry class even more than he now too often does, and grind up at home, it is difficult to see. But that it will be useful to the unfortunate demonstrator who is expected to teach practical chemistry to perhaps thirty men all at once, is quite evident. This is the real use of such illustrated books; and Dr. Hake lets the cat out of the bag in his preface, when he says: "The book, I believe, should prove of service in schools, or in large classes where individual attention from the teacher becomes difficult, or almost impracticable; and medical students who, under the present regulations, have a good deal of simple analysis to learn in a comparatively short space of time, will possibly find their labours lightened by its use." There is no doubt that all those hospital and school teachers who like to take the least possible trouble over their work will find it well worth their while to quietly introduce Dr. Hake's illustrated tables to the notice of the class. Like many such books, it is here and there a little slipshod, as witness the paragraph on metals, in which a student, having been told that he must not use HCl, but nitric acid, to dissolve Pb, Hg, and Cu, is yet left in doubt as to whether he might not use hydrochloric acid for Ag. Surely it would have been just as easy to put the Ag in the nitric acid set and be done with it. So far as the colouring goes, it is really very well done indeed, and quite amusingly natural in many cases, and as we said before, the book is a real boon to the overworked or lazy teacher, and to the "wagging" student.

### LAW NOTES.

**CONDENSED SKIM MILK.**—An oilman named White, carrying on business in Camberwell-road, was summoned at Lambeth Police Court, for selling condensed milk not of the substance and quality represented, according to the terms of the Adulteration Act.—Mr. Biron, barrister, instructed by Mr. Marsden, vestry clerk of Camberwell, appeared to prosecute; the defendant was represented by Mr. Besley.—George Dewey, one of the inspectors of the Camberwell Vestry, stated that he went to the defendant's shop and asked for three tins of condensed milk. White asked him what brand he would have, and he replied the "Standard" brand. There were several other brands there. He paid 9d. for the three tins. Witness now produced the certificate of Dr. Bernays, the analyst for Camberwell, which showed that 90 per cent. of the cream had been abstracted.—Dr. Bernays in his evidence stated that the certificate produced was given by him. The label upon the tins sold was as follows: "The Standard Brand is specially prepared from the richest cow's milk from which a portion of the cream has been removed, and nothing added but cane-sugar. It is better and cheaper than fresh milk for ordinary purposes. Five parts of water to one of milk, and for infants 8 to 15 parts water, according to age." There had been nothing added to the milk but cane-sugar.—By Mr. Biron: Such a preparation so diluted would not be fit food for infants.—Mr. Besley said the "Standard" brand was a good milk, and then proceeded to quote several decisions with regard to such cases, and contended that the defendant was not liable.—The defendant was called and stated that he sold the milk in question and other brands at 3d., 4d., 4½d., and 5½d. He declared that he told the inspector it was partly skimmed, and was sure he called the attention of the officer to the labels on the tins, which showed it was skimmed milk.—Some legal arguments followed, and Mr. Biron (the magistrate) said it no doubt was an important and difficult case. Under all the circumstances, however, he felt bound to convict, although at the same time he was fully satisfied the defendant was without the slightest blame or had any intention to defraud. He should, therefore, only be too willing to grant a case for the various points to be argued in a superior Court. He considered the sale was one to the prejudice of the purchaser under the Act, and he therefore ordered defendant to pay a fine of 20s. and costs.—Notice of appeal was given.

### CORRESPONDENCE.

*[The Editor is not in any way responsible for opinions expressed by his correspondents.]*

*To the Editor of the ANALYST.*

SIR,—In your current issue you are correct in ascribing to me the first mention in your columns of the phenolsulphonic test for nitrates and the naphthylamine test for nitrites in water (Vol. x., p. 199; Vol. xii., pp. 50, 152). It will be seen by reference to my papers that the extract from Dr. Leffmann's book approaches very nearly to a copy of my words. The same weights are given for preparing the reagents, and the same precautions directed to be observed. The only practical differences I have noticed are, the introduction of a glass rod with which to stir the mixture, and an error in the chemical formula.

I am, etc.,

Phoenix Mills, Dartford.

A. PERCY SMITH.

October 3rd, 1889.

# THE ANALYST.

DECEMBER, 1889.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A MEETING of the Society was held at Burlington House on Wednesday, the 13th ult., the President, Mr. Adams, in the chair.

The minutes of the London meeting in June and the Liverpool meeting in August were read and confirmed.

Mr. W. H. Collins, Analytical Chemist, of Bolton-le-Moors, was proposed as a member.

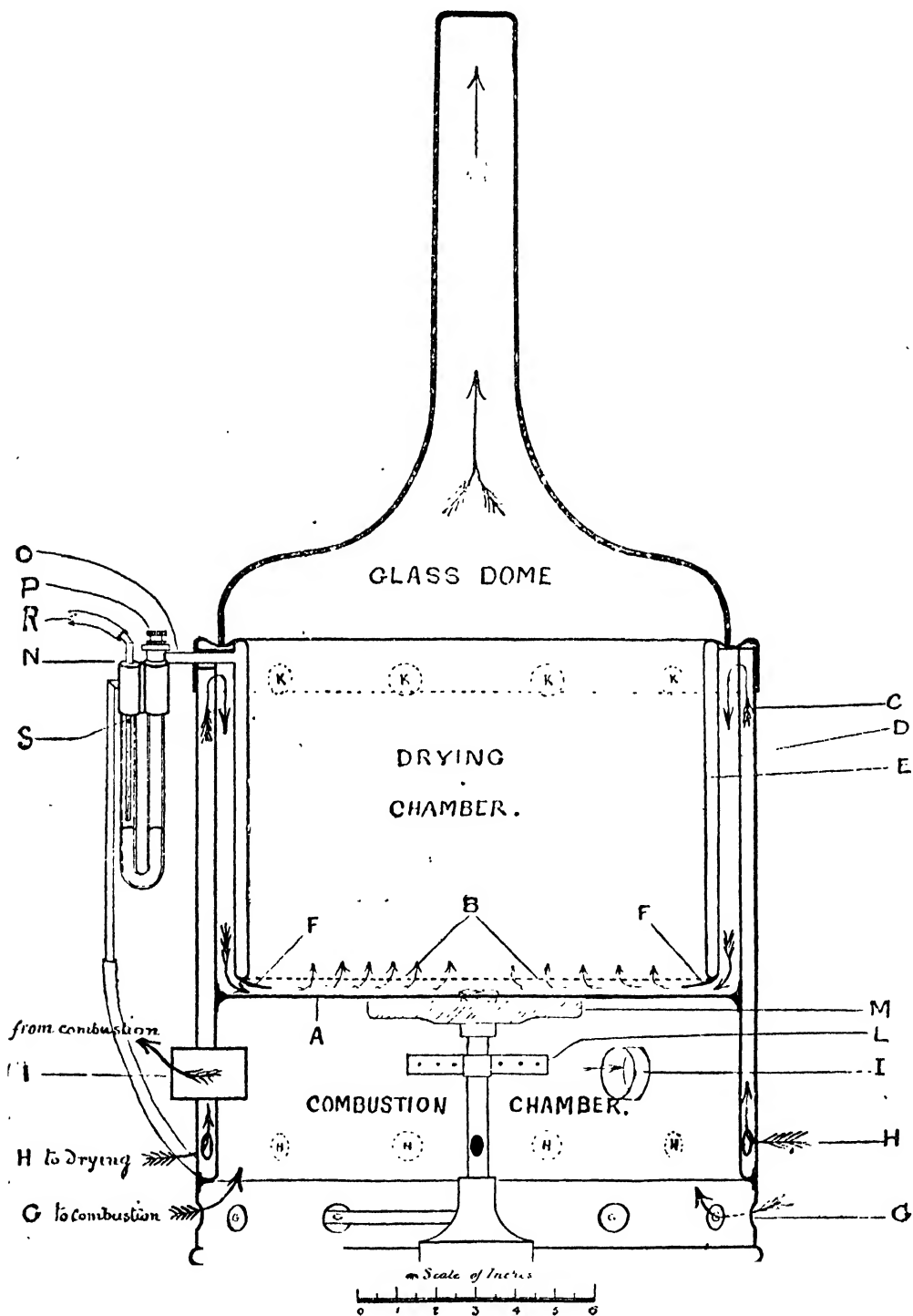
Mr. ADAMS read a paper "On a New Form of Air-bath," a model of which he exhibited and explained.

Mr. ALLEN read a paper "On Possible Future Extensions of the Duties of Public Analysts."

A prolonged discussion ensued on this, and ultimately, on the proposal of Dr. Muter, seconded by Dr. Johnstone, it was resolved "that Mr. Allen's paper be printed and circulated with the agenda for the next meeting, and that the discussion be adjourned until that meeting."

A paper by Dr. H. Leffmann and W. Beam, "On Some Applications of Centrifugal Action to Laboratory Work," was also read.

The next meeting of the Society will be held on Wednesday, the 11th inst., at 8 o'clock.



A. Diaphragm completely separating the drying from the combustion chamber. B. Perforated false bottom. C. Outer jacket. D. Inner jacket. E. Copper regulating chamber or thermostat. F. Baffle plate. G. Apertures in jacket C giving admission to air for combustion. H. Apertures for the passage of air between the jackets for drying. I. One of three apertures for escape of products of combustion. K. Apertures in inner jacket D for passage of drying air. L. Burner. M. Thick metal plate for receiving heat of the flame. N. Mercury U tube. O. And its connection with copper regulator. P. Screw whereby the degree of heat is regulated. R. Gas supply. S. Tube with bye-pass.

I have already mentioned the capacity of this copper regulator is 1100 c.c., the coefficient of expansion for one degree Centigrade being .00367, the alteration of volume for a single degree of temperature at boiling point will be about three cubic centimeters (2.95). It is therefore plain we have here a means of regulation of the temperature of extraordinary sensitiveness, and accordingly we find we can command what practically amounts to a fixed temperature at any desired degree, and seeing that the copper regulator entirely surrounds the drying chamber and that the whole of the air employed in the drying process must of necessity sweep both its surfaces, exterior and interior, amounting to nearly half a (.4459) square metre in extent, it follows that no local currents can interfere with the accuracy of its working. You will agree, I am sure, that this is a grand point.

A Page's regulator, or any similar instrument, may be all very well in a still atmosphere, but where a current is concerned it is not unlikely to be at fault and thrown out of working from one cause or another, purely local, such for instance as being shadowed by an object in process of drying, or being placed where there is either an undue amount of current, or too little, or in an eddy. Our arrangement has a further advantage of occupying no space within the drying chamber. Having said this much respecting the principles involved in the design and the mode of construction, let us now pass to a consideration of its performances; but before doing this it will be as well to relate some particulars concerning difficulties encountered in connection with the regulator. When first set in action there was no getting a fixed degree of heat; the thermometer kept steadily mounting, degree by degree, without apparent cause. Naturally we looked for some escape of air from the chamber of the regulator, but the closest inspection failed to reveal any point at which escape could take place, and it was only by immersing the copper regulator in water and blowing through the tube attached that enabled us to discover several tiny leaks in the solder. After these were made good and the test repeated, the thermometer still recorded a constantly increasing temperature. Again and again we went through the process of searching for leaks, but all in vain. Fixity of temperature seemed impossible, when at last I observed some condensation of moisture within the U tube on the regulator side of the mercury. This at once gave the clue to the cause of the rise of temperature. Each time of immersing the regulator in the water, when search was being made for leaks, a small amount of moisture must have gained access into the interior, and this, as the temperature of the bath was raised to boiling point, became converted into steam and mingled with the contained air. So long as this moisture remained at the high temperature of the interior of the regulator, it exerted the vapour tension due to that temperature, but little by little a certain portion found its way into the U tube out of reach of the heat, and thereupon deposited its moisture by condensation on the sides of the tube, pro-



ducing of course a partial vacuum in the tube and thereby drawing in a fresh supply of hot moist air and steam, so that at last quite a considerable amount collected in the U tube.

Now, seeing that 1 c.c., of water at 15.5 C. will produce 1696 c.c. of steam at 100° at ordinary barometric pressure, there is no need to dwell further upon the cause of our difficulty, or the necessity for keeping the interior of the copper regulator quite dry. I hope to be pardoned this digression. My excuse is that addressing practical men like yourselves one is bound to put those who may desire to follow in a similar investigation on their guard against needless loss of time, trouble, and temper.

Now, with respect to the performance of this instrument as an air-drying bath, I have directed my experiments to the demonstration of three things:—

I. To show the existence of, and determine the amount of, current passing through the bath.

The passage of the current is roughly but abundantly demonstrated by holding a flame opposite any one of the twelve air inlets; you will observe how the air rushes in. Again, at the outlet the current is manifested by this mica whirlygig arrangement, which you observe sails round famously by the impact of the current.

I have attempted to measure the amount of air that passes through the instrument by means of an anemometer, and find that it travels along a chimney whose sectional area is 5.4119 inches at the rate of 204 feet per minute, from which I calculate that no less than 7.6875 cubic feet of air pass through the apparatus per minute.

II. The next point of importance was to ascertain that this current was evenly distributed throughout the whole sectional area of the drying chamber.

This equal distribution you will observe was contrived at by making the instrument circular and admitting the air at points placed at equal intervals all round, and by surrounding the lower part of the inner jacket with a curved flange projecting inwards, the object of which is to direct the current horizontally between the true and the false bottom, and so prevent its premature passage through the perforations of the false bottom before having had time to take up heat from the bottom plate, and by thorough mingling and mixing, preventing local inequalities of temperature.

That those designs work well can be demonstrated by the smoke of smouldering brown paper, which shows that the current spreads itself over the whole area; there is no creeping up the sides or centre, it seems to pervade equally the whole space.

III. The final point that we have thought it important to enquire into relates to the vertical distribution of the heat.

At one time I was strongly tempted to head this communication with the title of "A Perfect Air-bath," and should have ventured to do so but for the practical impossibility of obtaining a perfectly equal temperature from top to bottom. For a certain very considerable range it is sufficiently so for all practical purposes, and far more so than it is, or can be, in any ordinary bath. For the convenience, if not the necessity, of the case, the source of heat is applied to the bottom, and you will remember we have interposed a large mass of metal between the flame and the bottom for the purpose of moderating, storing, and distributing the heat; but, nevertheless, all parts in metallic connection therewith get hot by conduction more in proportion as they are near to the

source of heat. They in turn become radiators, and any object placed within near range of their radiation before the air current has had time to take up and distribute the same, gets more than its share of heat. Our experiments show that the useful range is anywhere above 3 ins. of the bottom. Below this undoubtedly the temperature increases rapidly, and more so the closer the bottom is approached. Above 3 ins., and for the whole of the rest of the drying-chamber the extent of the variation between any two parts does not amount to more than from 1° Centigrade.

In these several ways we have endeavoured to meet the requirements of a theoretically perfect bath.

We have contrived an instrument that provides a vigorous current of heated air of definite temperature under perfect control of a self-acting source of heat, and out of reach of contamination by the results of combustion.

Taken together, these results are, I submit, satisfactory, and show the instrument to be a substantial improvement on the ordinary air-bath, of sufficient value, I trust, to deserve your attention.

The following table exhibits the temperature as shown by two thermometers, one being fixed at 8 ins. from the bottom, which uniformly registered 100 degs. Cent., and the other at various distances as follows:—

| Distance in inches. | Temperature degs. Cent. | Distance in inches. | Temperature degs. Cent. |
|---------------------|-------------------------|---------------------|-------------------------|
| 10½                 | 100                     | 5½                  | 100                     |
| 10                  | 100                     | 4½                  | 100                     |
| 9½                  | 100                     | 4                   | 100½                    |
| 9                   | 100                     | 2½                  | 101                     |
| 8½                  | 100                     | 3                   | 102                     |
| 8                   | 100                     | 2½                  | 104                     |
| 7½                  | 100                     | 2                   | 106                     |
| 7                   | 100                     | 1½                  | 110                     |
| 6½                  | 100                     | 1                   | 115                     |
| 6                   | 100                     | ½                   | 124                     |
| 5                   | 100                     |                     |                         |

The metal portion of the apparatus was made by James Clinch, of 30, King Street, Maidstone, and the glass dome by Messrs. Powell, Whitefriars Glass Works, E.C.

#### DISCUSSION.

Mr. ALLEN (who had temporarily taken the chair) said they would be very glad to inspect more closely this very ingenious and next door to perfect air-bath which Mr. Adams had described. They were indebted to Mr. Adams for several ingenious and practical devices. They would always associate his name with the paper-coil method of determining fat in milk, and they knew how thoroughly satisfied they were with it.

He would like to know how long it took before the desired temperature was obtained, because it was so extremely sensitive that the regulation of it might, he thought, prove troublesome in practice. He thought Mr. Adams might make the temperature more equable than it was by having an asbestos card-board diaphragm between the source of heat and the copper cylinder.

The contrivance by which Mr. Adams got rid of the heat afterwards was very interesting, because he got a good flow of heat over the bottom. He should have thought it was not necessary to have so large a copper cylinder to go over the interior of the bath, as it had a tremendous surface.

They were also indebted to Mr. Stansell for rigging up the apparatus there, and he should like to know where to get such glass hoods ready made, and he asked if it would not be convenient to have a regulator of the current, by means of a kind of damper at the top.

Dr. MUTER said he thought this would turn out a very useful improvement in laboratory apparatus. It was practically an ingenious circular modification of the principle of Griffin's air-bath, which he had used for many years, and which was doubtless at present the best bath in the market; the air being taken in at the top, entering the inner chamber through holes at the bottom, and finally escaping by the chimney. He had much improved the working of his bath by placing a sheet of asbestos mill-board over the bottom plate against which the burner impinged, and he thought, if the President would try such an addition, he would find that the unduly high temperature on the gauge bottom would no longer exist. If to this were added a second internal gauge, say two inches above the bottom one, for articles to rest upon, he should fancy that in the President's bath chemists would find the nearest approach to perfection yet met with in such apparatus.

Dr. VIETRI said that Griffin's bath, so far as he knew, was at the present time the best in the market. He had used it for nine years with very little trouble and good results. He would like to ask Mr. Adams whether it would not be advantageous to place the false bottom three inches above the present one; that is to say, at a height where the temperature, according to Mr. Adams' observations, was, so to speak, normal.

Mr. ADAMS, in reply, said that it was by no means an expensive or complicated affair, and they must remember that it was not only a bath, but a thermostat as well, and perhaps it was the copper chamber which constituted the thermostat that made it appear somewhat complicated. All the rest was plain enough. In every instrument that he had seen, the means for escape of the products of combustion of the gas used for heating, was placed below the inlet for the air used for drying. This was a very serious fault. They could see (as he showed) what an enormous amount of watery vapour came out by the outlets provided for the escape of these products, and in the ordinary bath this went straightway into the drying-chamber, to say nothing of carbonic acid. Replying to Mr. Dyer as to whether there was any reason for having the dome made of glass, Mr. Adams said it was really a mournful thing to him that through the model having been broken by the railway company he was unable to show it in its entirety; the glass not only looked well, but everything that was going on could be seen, and the drying process watched without disturbance; but, of course, the glass dome could be replaced by a metal one.

As regarded regulation of temperature, this was as simple as possible. It could be set at any temperature wished for, from that of the room up to any degree that could be required, in the course of a few minutes. He had only to undo the screw (P) and allow a little of the air contained in the copper chamber to escape, and when the desired temperature was reached, screw it down again, and this, by preventing further escape, fixed the temperature at that point. On the other hand, if he wanted to lower the temperature, he would turn the gas out and allow air to enter the copper chamber until the temperature stood at the desired point. A thermometer hung from the chimney, and the temperature could be seen at any moment. The regulation could be accomplished not only exactly but immediately, and, moreover, the temperature was absolutely fixed. It might be set going on January 1st and go on to December 31st, and it would not vary. It might do some good to put some asbestos on the upper surface of the diaphragm that divides the drying and combustion chambers.

*(Conclusion of the Society's Proceedings)*

## ON THE DETERMINATION OF CHLORINE IN WATER.

BY ALLEN HAZEN.\*

CHLORINE is almost always determined in water by titration with silver nitrate solution, using potassium chromate as indicator. It has been my practice to titrate fifty cubic centimeters of water or sewage in a porcelain dish with a silver solution of such strength that one cubic centimeter corresponds to half a milligram. of chlorine so that each cubic centimeter used represents one part of chlorine in 100,000. The results commonly obtained by this method are somewhat too high, owing to the fact that the red colour of silver chromate does not become perceptible until a certain excess of silver has been added, and this excess, as will be shown, is much too large to be neglected when close work is desired.

I have made a large number of experiments to ascertain the amount of excess of silver solution required to give an end-point under various conditions of titration, and especially to find the influence of the volume of the liquid titrated, the amount of chromate used, and the amount of precipitated silver chloride present. I have found that under constant conditions the required excess is constant, and that by making the proper corrections very accurate results can be obtained, even in widely differing conditions of titration.

The general method by which these experiments have been carried out is as follows : Silver and chlorine solutions were made by dissolving the theoretical quantities of pure silver nitrate and sodium chloride in distilled water. A solution of potassium chromate, free from chlorine, was used which contained 0.12 gram. per cubic centimeter. Measured quantities of chlorine and chromate solutions were put into a white porcelain dish with distilled water, and titrated with the silver solution. The amount of silver solution required was in every case more than an equivalent of the salt used. The excess is the amount of silver solution required to reproduce an end-point under the conditions of the experiment. In all cases I have not gone beyond an end-point which was as faint as could be seen with certainty after some seconds, there being always a second dish of chromate, for comparison, by the side of that in which the titration is made. The solution should not be so concentrated as to make the precipitated silver chloride coagulate, as in that case the required excess is somewhat greater than otherwise.

The amount of chromate used has a considerable influence on the result, especially in a large volume. In general, it may be said that the greater the amount of chromate used, the smaller will be the required excess of silver ; but when the quantity has reached a certain point, the advantage gained by any further increase is more than overcome by the increase in colour, which obscures the exact end-point. I have found 0.0010 gram. potassium chromate per cubic centimeter of liquid titrated (a much larger amount than is generally recommended) to be a suitable quantity. This is enough to give most of the advantage due to increased quantity, while the end-point remains very sharp. In practice I use 0.06 gram. of potassium chromate in all cases, even when the volume of liquid titrated is small ; the end-point is quite as sharp as with a smaller quantity.

\* American Chemical Journal.

The following titrations show the excess of silver solution required when different quantities of chromate are used, all other conditions being the same :

| NaCl sol.<br>taken. | K <sub>2</sub> CrO<br>grams. | Vol. of liquid<br>titrated. | AgNO <sub>3</sub> sol.<br>required. | Excess. |
|---------------------|------------------------------|-----------------------------|-------------------------------------|---------|
| 2 c.c.              | ·004                         | 50 c.c.                     | 2·45                                | ·45     |
| "                   | ·008                         | "                           | 2·35                                | ·35     |
| "                   | ·016                         | "                           | 2·27                                | ·27     |
| "                   | ·030                         | "                           | 2·20                                | ·20     |
| "                   | ·060                         | "                           | 2·16                                | ·16     |
| "                   | ·120                         | "                           | 2·15                                | ·15     |

The volume of the liquid titrated has also an influence on the result. (The volume may be easily determined, after titration, by pouring the liquid into a graduate.) The required excess of silver solution increases regularly with the volume, and when 0·06 gram. chromate is used, and the volume is not more than 60 c.c., this excess may be represented by the formula  $x = .003 v + .02$ , where  $v$  is the volume of liquid at the end of the titration in cubic centimeters. Thus with a volume of 3 c.c. the correction is ·03 c.c., while with a volume of 50 c.c. the correction is ·17 c.c.

The following titrations were made in different volumes, all other conditions being the same :

| NaCl sol. taken. | K <sub>2</sub> CrO <sub>4</sub> used. | Vol. of liquid. | AgNO <sub>3</sub> sol. required. | Excess. |
|------------------|---------------------------------------|-----------------|----------------------------------|---------|
| 2 cc.            | ·06 gr.                               | 4 cc.           | 2·03 cc.                         | ·03 cc. |
| "                | "                                     | 10              | 2·05                             | ·05     |
| "                | "                                     | 20              | 2·07                             | ·07     |
| "                | "                                     | 30              | 2·10                             | ·10     |
| "                | "                                     | 40              | 2·14                             | ·14     |
| "                | "                                     | 50              | 2·17                             | ·17     |
| "                | "                                     | 100             | 2·35                             | ·35     |

The amount of precipitated silver chloride present influences the result. The required excess of silver solution, in addition to the correction for volume, increases regularly with the amount of precipitated silver chloride, and is nearly proportional to the amount of silver solution used. The correction is nearly one per cent. of the volume of the silver solution. The most convenient way to apply this correction is to use a silver solution containing one per cent. more than the theoretical amount of silver. If the silver solution is standardised against sodium chloride, it will be of this strength, and no correction will be required for the amount of precipitate. If the amount of chlorine titrated is very low the results are somewhat irregular, so that if less than 1 c.c. of silver solution is required for 50 c.c. of water, I prefer to run in 1 c.c. of salt solution and deduct the equivalent of silver solution from the result. The influence of the amount of precipitated silver chloride is shown by the following titrations :

| NaCl sol. taken. | K <sub>2</sub> CrO <sub>4</sub> used | Vol. of liquid. | AgNO <sub>3</sub> sol.<br>required. | Excess. |
|------------------|--------------------------------------|-----------------|-------------------------------------|---------|
| 0·0 cc.          | ·06 gr.                              | 50 cc.          | ·10 cc.                             | ·10 cc. |
| ·2               | "                                    | "               | ·30                                 | ·10     |
| ·6               | "                                    | "               | ·72                                 | ·12     |
| 1·0              | "                                    | "               | 1·16                                | ·16     |
| 2·99             | "                                    | "               | 3·17                                | ·18     |
| 5·98             | "                                    | "               | 6·19                                | ·21     |
| 9·97             | "                                    | "               | 10·22                               | ·25     |

The silver solution used for these tritrations was very carefully made to contain exactly the theoretical quantity of silver. A portion of this solution was precipitated with its equivalent of salt solution; to the clear liquid, separated from the precipitate, was added a small amount of salt solution and chromate, and titrated with silver solution. The amount required was the same as when distilled water was used, all other conditions being the same.

Although the original silver solution was made by dissolving the theoretical quantity of pure silver nitrate in water, it is practically more convenient and better to depend upon titrations of salt solution for its strength, always making the correction for volume. As has been shown, a solution made in this way will require no correction for precipitated silver chloride, but the correction for volume must invariably be applied. As this correction is not at all proportional to the amount of silver solution used, accurate results cannot be obtained by using a stronger solution and omitting this correction.

A few titrations of salt solution in varying amounts of water, taken at random from my note-book, are as follows. The silver solution used was standardised against salt solution, and the correction for volume made. In each case .06 gram. chromate was used.

| Milligrams.<br>Cl taken. | Vol. of liquid.<br>cc. | AgNO <sub>3</sub> sol.<br>required. | Corrected for<br>volume. | Milligrams.<br>Cl found. |
|--------------------------|------------------------|-------------------------------------|--------------------------|--------------------------|
| 5                        | 16                     | 10.06                               | 9.99                     | 4.995                    |
| 5                        | 50                     | 10.18                               | 10.01                    | 5.005                    |
| 1                        | 40                     | 2.12                                | 1.98                     | .99                      |
| 1                        | 70                     | 2.20                                | 1.99                     | .995                     |
| .94                      | 80                     | 2.10                                | 1.84                     | .92                      |
| 1.53                     | 46                     | 3.26                                | 3.10                     | 1.55                     |
| 1.30                     | 30                     | 2.75                                | 2.64                     | 1.32                     |
| .87                      | 4                      | 1.76                                | 1.73                     | .865                     |
| 2.21                     | 45                     | 4.62                                | 4.47                     | 2.235                    |
| 9.20                     | 65                     | 18.70                               | 18.18                    | 9.24                     |
| 3.76                     | 22                     | 7.68                                | 7.59                     | 3.795                    |
| .46                      | 60                     | 1.10                                | .90                      | .45                      |
| 3.15                     | 35                     | 6.46                                | 6.34                     | 3.17                     |
| 1.65                     | 50                     | 3.45                                | 3.27                     | 1.635                    |

It is possible, by direct titration in this way, to get results within .05 part chlorine per 100,000 in clear waters, when the chlorine is not higher than 10 parts. When the chlorine is low and greater accuracy is required, the water must be concentrated before titration. When this is done, there must invariably be added an excess of sodium carbonate before evaporation, as otherwise there may be a serious loss of hydrochloric acid, even if the residue is not allowed to go to dryness. Commonly 0.02 gram. of sodium carbonate, or less, is sufficient, and this quantity does not in the least interfere with the titration. If too much has been used, calcium nitrate may be added before titration. An excess of nitrate does not influence the result.

I have concentrated waters in three ways, any one of which gives perfectly reliable results. First, by boiling down 500 c.c. or more in a flask with sodium carbonate, to about 50 c.c. By this method there is no possibility of hydrochloric acid being absorbed from the air. It is very convenient, and gives good results when there is not too much organic matter present. In such cases the residue becomes too brown for sharp titration, and must be decolorised by aluminium hydrate and filtered.

Second, by evaporation on a water-bath with sodium carbonate, to a small bulk.

Third, by treating the solid residue of evaporation. All determinations of solids in this laboratory are made with the addition of sodium carbonate, and the ignition is made in a radiator. I have found by a large number of determinations that there is no loss of chlorine whatever by igniting in this way, while all organic matter is destroyed. After the residue is weighed, the chlorides may be extracted with hot water, and transferred to a porcelain dish and titrated. When much organic matter is present, this seems to be the most accurate method, and in all cases it is very convenient. Care must be taken that no hydrochloric acid is absorbed during evaporation, and that all chlorine is washed from the residue.

The following determinations are given as illustrations of the different methods, and the correction for volume :—

| Serial No. | Amount taken. | Vol. of liquid. | NaCl sol. used. | AgNO <sub>3</sub> sol. required. | AgNO <sub>3</sub> corrected for vol. | Parts per 100,000. | R. marks.                   |
|------------|---------------|-----------------|-----------------|----------------------------------|--------------------------------------|--------------------|-----------------------------|
|            |               | 55              | 10              | 10.20                            | 10.02                                |                    | Standardisation.            |
| 2691       | 50            | 53              | 1 c.c.          | 1.30                             | .12                                  | .12                | Direct titration.           |
| "          | 500           | 45              | 0               | 1.53                             | 1.38                                 | .138               | Boiled down in a flask.     |
| "          | 250           | 20              | 0               | .80                              | .72                                  | .144               | Evaporated on a water-bath. |
| "          | 250           | 15              | 0               | .74                              | .68                                  | .136               | Solid residue.              |
| 2689       | 50            | 53              | 1               | 1.35                             | .17                                  | .17                | Direct titration.           |
| "          | 500           | 50              | 0               | 1.65                             | 1.48                                 | .148               | Boiled down in a flask.     |
| "          | 250           | 20              | 0               | .80                              | .72                                  | .144               | Evaporated on a bath.       |
| "          | 200           | 15              | 0               | .65                              | .59                                  | .147               | Solid residue.              |
| 2794       | 50            | 53              | 1               | 1.50                             | .32                                  | .32                | Direct titration.           |
| "          | 100           | 15              | 0               | .75                              | .68                                  | .34                | Solid residue.              |
| 2809       | 50            | 56              | 0               | 5.40                             | 5.21                                 | 5.21               | Direct titration.           |
| "          | 100           | 30              | 0               | 10.55                            | 10.44                                | 5.22               | Solid residue.              |
| 2821       | 50            | 58              | 0               | 7.53                             | 7.34                                 | 7.34               | Direct titration.           |
| "          | 50            | 20              | 0               | 7.38                             | 7.30                                 | 7.30               | Solid residue.              |

No. 2691 is a sample of the city water of Lawrence; No. 2689 is a sample of city water filtered through sand; Nos. 2794 and 2809 are other clear waters, and No. 2821 is a sample of sewage.

I have made duplicate determinations of chlorine by two or more of these methods in several hundred samples of water and sewage, with exceedingly regular results, and there appears to be no source of constant error.

Lawrence Experiment Station, Mass. State Board of Health.

## DYNAMICAL THEORY OF ALBUMINOID AMMONIA.

BY ROBERT B. WARDER.

(Continued from page 216.)

Curves of similar properties express the progress of other reactions which take place during concentration in large excess of reagents. Equations of the following forms are obtained by varying the exponent of  $x$  in equation (3) and using the appropriate constants. For reactions involving the concurrence of two molecules only,

$$-\log \frac{z_{\infty} - (y+z)}{z_{\infty}} = A \cdot \log \frac{z}{x_0} \quad (6)$$

For three molecules,

$$-\log \frac{z_{\infty} - (y+z)}{z_{\infty}} = A \frac{x_0 - x}{x} \quad (7)$$

For four molecules,

$$-\log \frac{z_{\infty} - (y+z)}{z_{\infty}} = A \frac{x_0^2 - x^2}{x^2} \quad (8)$$

In all such cases the formation of ammonia may take place most rapidly in the early, middle, or latter part of the distillation, according to the value of  $A$ .

If the ammonia, instead of appearing directly, is the final product of a succession of different reactions, a complete theory must take account of the gradual formation and disappearance of the intermediate products. Some evidence on this point will appear in section VI.

#### IV. Distillation of Albuminoid Ammonia.

Equation (1) applies to the distillation of ammonia only when the total quantity  $(y+z)$  remains constant; otherwise we must write  $-dz$  in place of  $dy$ . Thus,

$$\frac{-dz}{dx} = k \cdot \frac{y}{x}, \quad (9)$$

or

$$y = -\frac{x}{k} \cdot \frac{dz}{dx} \quad (10)$$

Substituting in equation (7),

$$-\log \left( 1 + \frac{xdz}{kz_x dx} - \frac{z}{z_x} \right) = A \frac{x_0 - x}{x} \quad (11)$$

This equation (as soon as a fixed value is given to  $A$ ) expresses a perfectly definite relation between the ammonia distilled and the volume remaining in the retort. It is not easy, however, to obtain an integral in form suitable for computation, and an indirect method was used. The ordinates of curve  $B$  represent the sum of  $y$  and  $z$  when  $A = 1$ ; these ordinates were divided into two parts, in accordance with the condition implied in equation (9). Curve  $D$  thus represents the gradual increase of  $z$ , and curve  $E$  shows the increase and subsequent decrease of  $y$ . A few corresponding points of these three curves are also indicated in the following table, increments of  $z$  being placed under the symbol  $\Delta z$ . These increments are shown on the figure as  $d$ ,  $d$ ,  $d$ . For convenience,  $z_{\infty}$  is taken as unit of weight for ammonia, and  $x_0$  is made equal to 8; as when a volume of 400 c.c. is distilled in fractions of 50 c.c. each. The ratio of each increment to the next is stated under  $r$ .

| $x$ . | $y+z$ . | $y$ . | $z$ . | $\Delta z$ . | $r$ . |
|-------|---------|-------|-------|--------------|-------|
| 8     | 0.000   | 0.000 | 0.000 | ..           | ..    |
| 7     | 0.280   | 0.129 | 0.151 | 0.151        | 0.58  |
| 6     | 0.535   | 0.122 | 0.413 | 0.262        | 1.05  |
| 5     | 0.749   | 0.087 | 0.662 | 0.249        | 1.31  |
| 4     | 0.900   | 0.047 | 0.853 | 0.191        | 1.74  |
| 3     | 0.978   | 0.015 | 0.963 | 0.110        | 3.23  |
| 2     | 0.999   | 0.002 | 0.997 | 0.031        | ..    |
| 0     | 1.000   | 0.000 | 1.000 | ..           | ..    |

When  $A = 1$  (as in this table),  $y$  reaches a maximum when  $x = 6.7$ , during the collection of the second fraction of distillate; and this fraction contains the largest quantity of ammonia. The third fraction contains nearly the same amount, but later increments show a rapid decrease. The large increase of ammonia indicated for the



second measure is due in very small part to the increased concentration of the permanganate, but chiefly to the fact that sufficient time has elapsed for the accumulation of ammonia in the retort. An increase in the second measure has been rarely observed in practice, except in a few experiments on pure chemicals, such as urea, theine, glychocholic acid, and notably in cyanuric acid. In the 59 samples of natural waters already referred to, the first measure always contained as much as  $1\frac{1}{3}$  times that found in the second; in 11 instances the ratio is 2, and in 33 instances it is more than 2. On the other hand, instead of an increase in this ratio for succeeding portions (as indicated by theory for a single reaction), it usually decreases, the ratio of the last two determinations being from 1 to 2. This want of agreement between the theory for a single reaction and observations on a natural water are exactly what we should expect; for the water may contain a great number of different substances, each undergoing change according to equation (6), (7), or (8), so that the actual rate of distillation depends upon the sum of the ammonia derived from all these sources. As curve E shows a rapid rise from zero to a maximum, followed by a gradual decrease to zero, so we may conceive a multitude of similar curves, with their several maxima at various points, but with a large share of them near the origin; implying  $A > 1$ , for the most part. The resultant of all such curves might have a single maximum, like the type given, or it might have a succession of maxima and minima. On the theory of averages, the former seems more probable. This resultant curve might have a great variety of forms in details, answering to the various behaviour of different waters.

#### V. *Extrapolation Formula for Residue in Retort.*

Many chemists, feeling that the task is not completed by nesslerising three measures, have pushed the distillation much farther. Mallet suggests a certain limit as criterion when the distillation has been carried far enough. If the ammonia found in the successive portions is reported, we can rudely plot the curves for ammonia distilled, ammonia in retort, or total ammonia formed. Each of these curves may be the resultant of many similar curves having different parameters. Can we find an empirical equation for the resultant that will conform to the analytical results, and thus enable us to apply a probable correction for the ammonia that would be obtained if the distillation were completed?

We may assume a curve of the form

$$y = Ax + Bx^2 \quad (12)$$

to indicate the varying quantity of ammonia in the retort under the condition that this is all distilled away when the fluid is gone. Substituting in equation (9),

$$\frac{-dz}{dx} = kA + kBx.$$

Integrating between the limits  $z_1$  and  $z_2$ ,

$$z_2 - z_1 = kA(x_1 - x_2) + \frac{1}{2}kB(x_1^2 - x_2^2);$$

or, for brevity,

$$\Delta_1 z = kA\Delta_1 x + \frac{1}{2}kB\Delta_1 x^2. \quad (13)$$

In like manner, for a second increment of  $z$  and for the undetermined portion,

$$\begin{aligned} \Delta_2 z &= kA\Delta_2 x + \frac{1}{2}kB\Delta_2 x^2, \\ \Delta_x z &= kA\Delta_x x + \frac{1}{2}kB\Delta_x x^2. \end{aligned} \quad (14)$$

Those who follow Wanklyn's directions for 500 c.c. of water begin the distillation of albuminoid ammonia with 350 c.c. of fluid, and distil three measures of 50 c.c. each, rejecting the last 200 c.c. Taking 50 c.c. as unit of volume,  $x_1 = 6$ ,  $x_2 = 5$ , and  $x_3 = 4$ , while  $\Delta_1 z$  and  $\Delta_2 z$  represent the ammonia found in the second and third measures. Assume  $z = r\Delta_2 z$ , then

$$\begin{aligned} r \Delta_2 z &= kA(6-5) + \frac{1}{2}kB(36-25) = kA + 5.5kB, \\ \Delta_2 z &= kA(5-4) + \frac{1}{2}kB(25-16) = kA + 4.5kB. \end{aligned}$$

By elimination,

$$kB = (r-1)\Delta_2 z \text{ and } kA = (5.5 - 4.5r)\Delta_2 z.$$

But

$$\begin{aligned} \Delta_2 z &= 4kA + 8kB, \\ \therefore \Delta_2 z &= (14 - 10r)\Delta_2 z. \end{aligned} \quad (15)$$

If

$$r=1, \Delta_2 z = 4\Delta_2 z;$$

that is, if the second and third measures yield like quantities of ammonia, the best correction we can make is to assume that the distillation of four times 50 c.c. still remaining in the retort would yield four times that quantity.

If  $r > 1\frac{1}{2}$ , the value of  $A$  becomes negative, and therefore  $y$  becomes negative for small values of  $x$ . This involves a physical impossibility, but we may meet the difficulty by treating the equation

$$y = Ax^2 + Bx^3 \quad (16)$$

in the same manner as equation (13), whence

$$\Delta_2 z = \frac{188 - 100r}{37} \Delta_2 z, \quad (17)$$

a correction which again fails if  $r > \frac{9}{10}$ .

We may test these formulas by means of Smart's experiments with pure chemicals; but, as we began the action with 400 c.c. of fluid instead of 350,  $\Delta_1 z$  and  $\Delta_2 z$  represent his third and fourth fractions, with the advantage of greater distance from the beginning of the operation, where equation (12) is wholly inapplicable. The available data (for values of  $r$  between 1 and 1.5) are given in the following table, which states under:—

- A, per cent. ammonia found in the first four fractions;
- B, per cent. ammonia found in "exhaustive experiments";
- C, per cent. ammonia obtainable after the first four fractions; and
- D, per cent. ammonia indicated by the extrapolation formulas.

|                                     | A.    | B.     | C.    | D.  |
|-------------------------------------|-------|--------|-------|-----|
| Silver and potassium cyanide, .. .. | 2.25  | [17.1] | 14.85 | 2.4 |
| Prussian blue, .. ..                | .3    | 25.8   | 52.5  | .2  |
| Urea, from urine .. ..              | 8.7   | 43.10  | 34.4  | 8.8 |
| Urea, from ammonium cyanate, .. ..  | 8.65  | ..     | 34.45 | 6.6 |
|                                     | 7.7   | 43.4   | 35.7  | 8.0 |
|                                     | 7.5   | ..     | 35.9  | 8.0 |
| Alloxan, .. ..                      | 6.55  | 21.3   | 14.75 | 2.5 |
|                                     | 6.6   | ..     | 14.7  | 2.4 |
| Thiocarbamilide .. ..               | 4.15  | 11.85  | 7.7   | 1.6 |
| Thiocarbamide, .. ..                | 15.25 | 22.50  | 7.25  | 1.7 |
|                                     | 15.0  | ..     | 7.5   | 1.6 |
|                                     | 4.0   | 5.4    | 1.4   | .4  |
| Strychnine sulphate, .. ..          | 3.75  | ..     | 1.65  | 1.0 |
|                                     | 5.0   | 5.32   | .32   | .5  |
| Codeine, .. ..                      |       |        |       |     |

\* To obtain a more general formula for the correction proposed, we may assume

$$y = Ax^n + Bx^{n+1}, \quad (18)$$

whence, by the same treatment illustrated above,

$$\Delta_\infty z = \frac{(\Delta_1 x^{n+1} - r \Delta_2 x^{n+1}) \Delta_\infty x^n - (\Delta_1 x^n - r \Delta_2 x^n) \Delta_\infty x^{n+1}}{\Delta_2 x^n \Delta_1 x^{n+1} - \Delta_1 x^n \Delta_2 x^{n+1}} \Delta_2 z, \quad (19)$$

where  $A$  is positive or zero when

$$r < \frac{\Delta_1 x^{n+1}}{\Delta_2 x^{n+1}}. \quad (20)$$

We may either make  $n$  the smallest integer consistent with the condition (20), or we may determine  $n$  by making the fraction equal to  $r$ . The function  $\Delta_\infty z = \phi(r)$  will be a smooth curve in either case, consistent with the theory as developed above and with the analytical results.

A glance at the last two columns shows that the ammonia actually obtainable after one-half of the fluid had been distilled was many times the proposed correction. An explanation of this discrepancy will next be considered.

#### VI. *Evidence of Intermediate Compounds of Nitrogen.*

Making some allowance for the difference between equation (7) (which was selected for study) and equations (6) and (8), it is safe to conclude from the table in section IV, that if the action of alkaline permanganate upon a pure compound of nitrogen could be represented by any single chemical equation (no matter how complex), we should have reason to expect this change to take place with such speed that fully 70 per cent. of the theoretical yield of ammonia would be obtained by distilling one-half the fluid, or else with such slowness that the first measure would contain far less ammonia than the second. Published experiments with at least eight bodies \* contradict both these conditions, and we are forced to believe that in the earlier stages some molecules of the original body yield ammonia with promptness, while others are converted into more stable forms and resist the action with great stubbornness. The nature of these intermediate products is not yet clear, except only that  $\alpha$  (as defined in section III.) is small, in their reaction with alkaline permanganate. Perhaps they may be chiefly condensation products. Alloxan, which yielded 4 per cent. ammonia in the first fraction (eighth) of distillate, and only 2.57 per cent. in the next three, but 21.3 per cent. by prolonged action, is a marked example of such behaviour; this, no doubt, is partly converted into parabanic acid. So, likewise, in a water analysis, many substances may yield a small part of their nitrogen as ammonia, while the greater part is converted into more stable forms which elude detection. It has been supposed that the organic matter of potable water is more like asparagine, yielding its nitrogen readily under the action of permanganate. Of this, however, I have found no proof. In about 40 per cent. of the natural potable waters referred to, the ratio of the third and fourth fractions is 1.5 or less, giving grave suspicion of incompleted action when the distillation was stopped. Even if the yield of ammonia in some fraction has fallen below the limit of delicacy in nesslerising, what evidence have we that prolonged treatment would not develop a much larger amount of ammonia than that already obtained?

#### VII. *Applications to the Analytical Process.*

A debt of gratitude is due to Professor J. Alfred Wanklyn, as the author of a valuable method of analysis which has done much in the interest of public health. "The ammonia process," which originated in 1867, is still described in the 7th edition of "Water Analysis" (1889) essentially as in the author's first paper upon the subject. In a process of such delicacy, where the results may be influenced by a multitude of variable conditions, it is desirable that these should be accurately defined and conscientiously followed. According to the author's latest directions, 500 c.c. of water are reduced to 300 c.c. (to remove free ammonia) and 50 c.c. of the reagent added; three measures of distillate are then collected, when "the distillation may be stopped . . . . It is necessary to nesslerise each separate 50 c.c. of distillate, and to add the amounts together, in order to arrive at the total albuminoid ammonia." Besides this process, a

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\* These are the first six named in the last table, besides parabanic acid and theine.

second is described upon a scale of one-fifth, with this important modification, that the operation is "continued so long as 10 c.c. of distillate shows a sign of ammonia"; if, then, with a delicate Nessler reagent, ammonia is found in the sixth measure of distillate, the fluid must be evaporated to dryness!

But why should 350 c.c. be distilled until only  $\frac{3}{4}$  have gone over, while 70 c.c. are distilled up to a very different limit? Probably because the *time* required to evaporate 30 c.c. from the smaller retort proved insufficient for both the chemical action required and for the separation of the ammonia. Professor Wanklyn's method, as conducted in his own laboratory and by his own hands, has doubtless done valuable service, yielding good comparable results; but more definite conditions must be adopted if we would avoid discrepancies among different places and persons. Its value depends upon giving constant and comparable results under fixed conditions. For the absolute estimation of organic nitrogen, it is worthless.

It will be instructive to divide the free or albuminoid ammonia found in each measure of distillate by that found in the next, and to record the ratio so found; especially if care is taken to boil at a constant rate. According to Smart,\* with pure animal or vegetable albuminoids,  $r=2$ ; but if these have passed into the putrefactive condition,  $r=3$ ; while in the case of urea (after the preliminary stage is passed)  $r=1$ , both for free and for albuminoid ammonia. The successful detection of recent sewage is reported, when the chemical evidence consisted in the persistent evolution of free ammonia, followed by persistent evolution of twice as much albuminoid ammonia.

The term "albuminoid ammonia," like "reverted phosphoric acid," has a technical significance determined by the method adopted in the analysis. The actual market value of reverted phosphoric acid cannot be so high under the rule for extraction at  $65^{\circ}$  as under the rule for extraction at  $40^{\circ}$ ; so also 0.1 mgm. of ammonia obtained by prolonged and intense action is of less real importance than the same quantity obtained by less vigorous measures. Many modifications of the original process have been proposed; among these Breneman's† are worthy of special consideration. If the fluid is brought nearly to dryness, as he suggests, it may be possible to apply an extrapolation formula, such as equation (19), to the measured residue. The detailed record of ammonia found in seven successive fractions (with greatly increased temperature and concentration at the last) may help to distinguish between different kinds of nitrogenous matter, yielding ammonia more readily and less readily; but care should be used in regard to the volume of the residue; if this is 4 c.c. in one case and 7 c.c. in another, there may be considerable difference in the oxidation of that comparatively inert matter which we have been led to suspect.

If the ammonia process should be applied to investigations of the relative stability of organic compounds,‡ the formulas given above may be adapted to numerous possible modifications. The use of return-flow condensor (to prolong the chemical action apart from distillation), and variations in the proportions of potash and permanganate, do not

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\* Public Health (Minn.), Vol. II, No. 3, May, 1886.

† Jour. Amer. Chem. Soc. 8, No. 9.

‡ It may be of interest to compare such results with those of Dreyfus, who studied the rate of oxidation with acid solution of permanganate Compt. rend. 105, 523.

seem to have yet been tried. It is difficult to see why the alkali should always be used in so much greater excess than the oxidiser (in spite of inconvenient bumping), but it is especially strange that the distinguished author, ignoring Mallet's report of 1882, and republishing his directions without any revision, should leave the important question of *time* entirely out of account. "Suffering persecution for the sake of the truth" should make the scientist keenly alive to any truthful criticism, and ready to study the contributions of his colleagues. The "ammonia process" has now passed from one laboratory into a hundred. If "discovered about a generation before chemists were prepared for it," the time is now fully ripe to collect the testimony of those who have used it; to agree upon the general conditions of quantity, rate of boiling, and limit of distillation, and even upon such details as the matter of paper or rubber connections. When a satisfactory compromise is effected we may hope to have a uniform method of procedure and a real definition of albuminoid ammonia.

#### REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

DEXTRIN IN GENUINE HONEY. C. AMTHOR AND J. STERN. *Zeitschr. f. angew. Chemie*, No. 20, 1889.—44·9655 grms. of a sample of undoubtedly genuine honey were dissolved in 300 c.c. of water and allowed to ferment with yeast. After filtering and making up to 200 c.c., the liquid was examined in a Laurent's polariscope, and gave  $+24\cdot9^\circ$  in a 20 c.m. tube. The dextrin was then converted into dextrose, by heating 100 c.c. of the liquid with 10 c.c. of hydrochloric acid for three hours in a water-bath. After cooling and making up again to 100 c.c., the polarisation gave  $9\cdot21^\circ$ , equal to 2·249 per cent. of dextrose. Allihn's gravimetric sugar process gave 2·266 per cent. The formation of dextrose points to the honey having contained dextrin. The authors further confirmed this view by preparing phenylglycosone. A large quantity of honey was fermented in a weak solution. The filtrate yielded on evaporation a brown thickish syrup, which was really an impure dextrin. After dissolving in a little water, phosphotungstic acid, containing some sulphuric acid, was added, and the liquid filtered. The excess of the reagent was removed by means of baryta water, and this in turn removed by cautious addition of sulphuric acid. After concentrating a little, liquor plumbi was added, the liquid filtered, and the excess of lead removed by hydrogen sulphide.

The filtrate was evaporated in the water-bath until it became a thin syrup, and 200 c.c. of 90 per cent. alcohol were added, which was sufficient to keep the dextrin in solution. After filtering and evaporating, the dextrin was obtained as a brown syrup, which was purified with animal charcoal, until it was finally got as a yellowish brittle amorphous mass. It is exceedingly soluble in water, very hygroscopic, soluble in spirits of wine, but insoluble in absolute alcohol or ether. The watery solution very slightly reduces Fehling's liquid.

5 grms. of this dextrin were dissolved in 200 c.c. of water, mixed with 20 c.c. of 20 per cent. sulphuric acid, and heated for three hours in water-bath. The liquid was neutralised with barium carbonate, filtered, and evaporated to a syrup, which was

repeatedly exhausted with alcohol. After distilling off a brownish syrup was obtained, which was purified by animal charcoal.

It crystallises in granules, reduces Fehling's strongly, and the authors succeeded in preparing phenylglycoson, by warming 1 grm. with 2 grms. of phenylhydrazin, 3 grms. of sodium acetate, and 20 c.c. of water. The crude product was recrystallised from alcohol and obtained in small yellow needles, fusing at  $204^{\circ}$  C. This removes all doubt about the original substance being dextrin, the presence of which in honey may perhaps be explained by the bees feeding, when they get the chance, on malt in breweries.

L. DE. K.

TREATMENT OF URANIUM RESIDUES. D. LAUBE. *Zeitschr. f. angew. Chemie*, No. 20, 1889.—The liquids resulting from the precipitation of phosphates with uranium salts are kept in a large vessel, and the supernatant fluid is occasionally drawn off. When a sufficiency of precipitate has collected, the whole is heated to boiling in an iron vessel, and common soda is added until the precipitate seems dissolved. After cooling, and without filtering, ammonia is added until the mixture smells perceptibly of it, and the phosphoric acid is then thrown down with magnesia mixture, prepared by dissolving equal quantities of magnesium and ammonium sulphates. After, say, twelve hours, the liquid is syphoned off, and the residue washed with ammoniacal water. The united filtrates are now neutralised, either with hydrochloric or sulphuric acids, and freed from carbonic acid by boiling. The uranium is now precipitated by ammonia, as uranic-ammonic oxide. This precipitate is washed by decantation, but it is advisable to put a small quantity of ammonium sulphate to the wash water.

By dissolving the precipitate in excess of nitric acid and evaporating, commercially pure uranic nitrate is obtained in crystals, which are allowed to drain on a funnel and washed with a very little cold water.

L. DE K.

ESTIMATION OF TANNIC ACID IN OAK BARK, WITH PERMANGANATE. F. GANTER. *Zeitschr. f. angew. Chemie*, No. 20, 1889.—The author found that tannin is completely and quantitatively oxidised by permanganate when its solution is mixed with dilute sulphuric acid and boiled. To estimate the tannin in a sample of oak bark, the following solutions are wanted: 1. The usual bark decoction, 10 grms. per litre. 2. A solution of permanganate, containing 3.988 grms. of  $K_2 Mn_2 O_8$  per litre. 3. A solution containing 7.951 grms. of oxalic acid per litre. 10 c.c. of the bark solution are mixed with 10 c.c. of dilute sulphuric acid, and heated to nearly boiling. Permanganate is now added, about 1 c.c. at the time, until the red colour but slowly disappears. The liquid is now once more heated to boiling, and permanganate is gradually added in excess, which causes a heavy brown precipitate. Oxalic acid is now run in until the liquid has become quite clear, and permanganate is then again added until red colour is restored. The total number of c.c.'s of permanganate used, less those of oxalic acid, is the amount reduced by the tannin, and at once represents the percentage of tannin in the sample.

It is of course advisable to repeat experiment after removal of tannin by hide powder as usual. The author is now engaged in trying to find out the exact relation between permanganate and the other kinds of tannic acid.

L. DE K.

## CORRESPONDENCE.

[The Editor is not in any way responsible for opinions expressed by his correspondents.]

To the Editor of the ANALYST.

## MILK ANALYSIS.

DEAR SIR,—In an article on "Milk Analysis" in the ANALYST of November, 1889, Dr. B. F. Davenport states that the fat can be *entirely* extracted from the dried residue of 5 grms. of milk, if only this be in a flat-bottomed platinum dish of  $2\frac{1}{2}$  inches diameter. He uses four separate quantities of boiling benzoline. Unluckily, he gives no comparative analyses to show that the fat is *entirely* extracted.

For years I used exactly the method described, sometimes with larger flat-bottomed dishes, and always with more numerous changes of benzoline, boiled on the residue. The fat, however, was never entirely separated, nor even to within "one tenth of a per cent." In a paper in the February number of the ANALYST, 1889, he will see this method contrasted with more modern methods. In my experience, there are only four methods that extract all the fat from a milk. 1st. Soxhlet's Areometric method. 2nd. Soxhlet's tube with pumice, plaster of Paris, kieselguhr, or paper-coil (Adams). 3rd. The Lactocrite. 4th. The Schmid method; this last was described in the *Chemical News*, of November 1st, 1889.

Yours faithfully,

ALF. W. STOKES, F.C.S. F.I.C.

Analytical Laboratory,

Vestry Hall, Harrow Road,

November 4th, 1889.

To the Editor of the ANALYST.

SIR,—I have read with extreme interest, Dr. Bennett F. Davenport's article upon Milk Analysis, as printed in your last issue. I thoroughly agree with him in all that he has written concerning the estimation of the fat in milk, the process employed, being termed by him a modified Wanklyn. I am in the habit of using platinum basins of  $2\frac{1}{2}$  inch diameter, but having quite flat bottoms, and have no difficulty whatever in obtaining a very thin and evenly distributed skin of residue, the complete extraction of which by means of petroleum ether, is easily accomplished. Petroleum ether as mentioned by Dr. Davenport, having a great advantage over that of ether in not dissolving either lactic acid or lactose. The process known as the "Adams blotting paper," and recommended by the Milk Committee of the Society of Public Analysts, is a process which I consider to be faulty, and that in three respects, and my reasons for saying so, are as follows:—

1st. You cannot estimate directly both the fat and the solids not fat. 2nd. That the amount of fat obtained is in excess of that originally present in the milk, owing to an increase in weight, due to rapid oxidation of the fat when in contact with cellulose, when spread over such a large surface, and also to a further oxidation which takes place when completing the drying of the extracted fat in the water oven. 3rd. It cannot be used when the milk is not fresh, objections which are, in my opinion, fatal to any milk process.

I used blotting paper in milk analysis in 1882 and relinquished its use owing to the last objection, and finally by a long series of experiments, satisfied myself as to the correctness of my second objection, and when coupling that with the first and the third objection, I have now no hesitation in rejecting it as faulty.

My opponents may say that the fat calculated from the sp. gr. and total solids, agree with that found by Mr. Adams' process, but to that I reply, we have already had examples of altering formula to suit the particular process employed.

I am, yours truly,

WILLIAM JOHNSTONE.

City Central Laboratory,

13, Fish Street Hill, E.C.

November 4th, 1889.

## APPOINTMENT.

Mr. J. Falconer King, Analyst to the City of Edinburgh, has been appointed Public Analyst for the County of Haddington.

ERRATUM. - On page 217, vol. xiv., line 2, after 1889, read "and *Jour. Soc. Chem. Industry*, September 1889."

# The Analyst,

INCLUDING THE PROCEEDINGS OF

THE "SOCIETY OF PUBLIC ANALYSTS."

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT OF THE  
ANALYSIS OF FOOD AND DRUGS, AND OF GENERAL  
ANALYTICAL AND MICROSCOPICAL RESEARCH.

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EDITED BY

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# THE ANALYST.

JANUARY, 1890.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

An ordinary meeting of the Society was held at Burlington House, on Wednesday, the 11th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

A ballot was taken for new members, and the following were declared to be duly elected:—As members, C. H. Cribb, B.Sc.Lond., F.I.C., F.C.S., public analyst for the Strand; W. Hepworth Collins, F.C.S., analytical chemist, Bolton. As associate, S. H. Collins, assistant to Mr. Young.

The following gentlemen were proposed for election:—W. Newton, Ph.D., F.I.C., F.C.S., analytical chemist, London; G. H. Masson, of Trinidad.

Mr. Turner and Mr. Cassal were appointed as auditors, to audit the accounts for the past year.

The adjourned discussion on Mr. Allen's paper on "Possible Future Extensions of the Work of Public Analysts," was then resumed and concluded.

The Annual Meeting of the Society will be held at Burlington House, on Wednesday, the 8th inst., and followed by the annual dinner, as usual.

## THE POSSIBLE FUTURE EXTENSION OF THE DUTIES OF PUBLIC ANALYSTS.

BY ALFRED H. ALLEN.

*(Read at the Meeting, November, 1889.)*

IN my Presidential Address, delivered at the annual meeting in January last, I called attention to the possibility of enlarging the sphere of action of public analysts. At present the duties of public analysts are well known to be restricted to the examination of food and drugs, and owing to the clause relating to the examination of articles purchased by private persons having proved nearly inoperative, a public analyst's duties are at present almost wholly limited to the examination of samples purchased for the purpose of analysis by inspectors acting officially. Even the analysis of water does not come within the official duty of public analysts, owing, as we are well aware, to the exclusion of drinking water from the operation of the Sale of Food and Drugs Act.

Owing to the publication of improved methods of analysis, to which the Society of Public Analysts has so much contributed, and to other causes with which we are all familiar, food analysis has acquired a position which none of us could have anticipated sixteen years ago. At the present time, the public analysts of the country are a body of highly competent men, whose special training, not only as analysts but as chemico-legal experts, specially qualifies them for executing the responsible duties of State chemists, and there are many new directions in which the public analyst might be employed to the advantage of the public.

It seems to me a grave public evil that the provisions of the Sale of Food and Drugs Act are not extended to include articles which do not come under the denomination either of a food or a drug. Thus, for instance, there have been successful prosecutions in some parts of the country for the sale of adulterated *olive oil*; but it seems to me doubtful whether olive oil comes under the Act, unless it is intended for use as a food or a remedy. That it is an article named in the British Pharmacopœia is not sufficient, for, unfortunately, when the Sale of Food and Drugs Act Amendment Bill was in committee in 1879, Dr. Bell advised that the British Pharmacopœia should not be formally adopted as the legal standard of all articles described therein. He did this on the ground of non-necessity, as the Pharmacopœia was already substantially regarded as the authority; but we all know how far this is from being the case in practice. Partly, this may be due to the very inefficient manner in which parts of the Pharmacopœia are edited; but if in a new Act the Pharmacopœia were made the legal Standard for drugs, such pressure would be brought to bear on the editors as would compel them to remove the blemishes which at present discredit their work.

It is very questionable, again, whether *yeast* can fairly be regarded as coming within the four corners of the existing Act, though any new Act should certainly be drafted so as to include it.

*Carbolic disinfecting powders*, again, are articles which are by no means always of the quality alleged. Corporations and Boards of Health suffer largely from deficient strength in the carbolic powders supplied to them; a powder sold as containing 10 per cent. of tar acids in reality often contains only 6 or 7 per cent., and sometimes

as little as 4 per cent., and the members of the general public are also very liable to get very poor value for their money and disinfectants of doubtful strength and efficacy.

*Petroleum*, again, is an article which might, with advantage, be occasionally submitted to public analysts. The Petroleum Act requires no alteration for this to be done, as it provides for the testing of the oil by the inspector "or other competent person selected by him," which person should be the public analyst for the district.

There ought also to be some definite control over the sale of articles containing *arsenic*, such as carpets and paper-hangings. If an Act were passed on the lines of the Margarine Act, enabling an inspector to visit shops where carpets and paper-hangings were sold, and to take for examination by the public analyst samples of any goods which were not *marked* as containing arsenic, the public would know what they were buying, and arsenical colours would soon be a thing of the past.

The same principle might be applied to *mixed fabrics*. All mixed fabrics should be labelled as such, the responsibility of labelling them to rest with the vendor.

I think that the inspectors under the Sale of Food and Drugs Act might be advantageously employed to see that the provisions of the Pharmacy Act are carried out, instead of leaving the matter, as at present, to the Pharmaceutical Society. The inspector should be instructed to ask for a *poison*, and see that the sale was properly recorded, and the name and address of the vendor entered in the Poisons Book.

It would also be a great advantage if it were enacted that all poisons sold as *vermin-killers* should be coloured with a definite proportion of some colouring matter, which could be easily detected and estimated. A few months since a man in Derbyshire poisoned his child with vermin-killer containing strychnine for the sake of the insurance money, and would not have been convicted and hanged but for the presence of a blue colouring matter in the vermin-killer. In connection with this case I received from the police a number of packets of vermin-killers containing strychnine, and I supplemented these by ten other samples, representing the chief wholesale manufacturers in the kingdom. The results of the analysis of these samples showed that ultramarine was the colouring-matter most commonly used, though Prussian blue occurred in several cases. Carmine was also present in several, and one specimen was wholly colourless, consisting merely of a mixture of strychnine and starch. In two other cases the colouring-matter was only sufficient to tinge them a very pale flesh or pink colour. One sample only was coloured with soot. It seems to be very important that vermin-killers should be so coloured as to preclude the chance of their being taken accidentally by human beings, and so as to facilitate their detection in cases where they have been swallowed, whether they may have been used for the purpose of suicide or murder.

At present, *arsenic*, if sold in quantities of less than 10 lbs., has, by law, to be coloured with soot or indigo, though it is a fact worthy of note that the solid arsenic found in the house of the late Mr. Maybrick was all coloured with wood-charcoal. Carbon, in any form, is not a suitable colouring-matter, as, in small quantities, and in presence of miscellaneous organic matter, it is difficult to identify, and indigo is too susceptible to oxidising and reducing agents to render it a desirable pigment. Prussian blue and ultramarine each have their disadvantages, and a mixture of indigo, Prussian blue and ultramarine would be better than either of these colouring-matters separately.



On the whole, perhaps, the most suitable pigment for colouring vermin-killers would be the oxide of chromium. In it we have a bright green pigment of high colouring power, quite insoluble in water and in dilute acid and alkaline liquids. It is wholly permanent under all imaginable conditions, and is not affected by ignition. Chromium is not a natural constituent of the body, is not used internally as a medicine, and is not liable to be present accidentally, even in traces, in any beverage or article of food. It can be detected and determined with ease and certainty, even when present in very minute quantity. Owing to its insolubility, oxide of chromium would remain wholly unabsorbed if taken internally. Hence, if it were added to preparations of strychnine in a definite and invariable proportion, say 20 per cent., an estimate of the *minimum* amount of poison taken by the deceased person could be arrived at by determining the quantity of chromium contained in the alimentary canal, even though the poison itself had been wholly absorbed or decomposed; and this could be effected with equal ease and certainty after prolonged inhumation, or even after cremation of the body.

But it would be useless to enact that all preparations of arsenic, strychnine, and other deadly poisons sold as vermin-killers should be coloured with a definite proportion of mineral pigment, if the sale of fly-papers, containing a dangerous or fatal dose of arsenic or other poisons, is to be permitted with impunity. All such fly-papers should be impregnated with some soluble colouring matter, which would colour the water in which they were soaked. But organic colouring matters are less suitable for the purpose in question than certain inorganic colouring matters. Of these the soluble salts of chromium present several advantages. Thus, if in the form of the double tartrate of chromium and potassium (or a mixture of chrome-alum and Rochelle salts) the chromium is not precipitated from its solution by alkalis, acids, sulphuretted hydrogen, sulphide of ammonium, or phosphates, or carbonates of the alkali metals. On the other hand, the chromium will not interfere with the detection and determination of arsenic, strychnine, and other poisons, and can be itself determined with ease and accuracy after evaporating the liquid to dryness and igniting the residue. Hence I hold that it is highly desirable that a law should be passed compelling the colouring of vermin-killers, fly-papers, etc., with an indestructible colouring matter, the quantity of which should bear some definite proportion to the active poison present; and I think public analysts might be advantageously employed to see that such a law, when passed, was enforced.

The directions indicated are only some of those in which it seems to me public analysts ought to look in the future for the extension of their duties. In fact, a public analyst of the future ought to become a State chemist, who should be officially consulted on all subjects within his province. There is much to be done before we can look forward to public analysts occupying such positions; but this is a greater reason for endeavouring to promote our ends. Personally, I have alluded to the desirability of extending the present acts relating to sanitary chemistry in several of my quarterly reports, and I believe some few other analysts have done the same, but I am afraid many public analysts have failed to recognise, or at least to use, the opportunity afforded by these quarterly reports of ventilating subjects of the kind.

We may accept it as certain that during the next Session of Parliament the Government will initiate some new legislation dealing with the sale of poisons; and the occasion may serve as an opportunity for urging on them the importance of making some modification in the Sale of Food and Drugs Act, and other laws relating to sanitary chemistry. It is highly important, therefore, that we should not wait for the Bill dealing

with the subject to be drafted by some one who will ignore our existence, as has happened on more than one occasion, but that we should ourselves draft a Bill embodying our views, and which may form the foundation of the legislation we hope for.

That the Society of Public Analysts can do much in the suggested direction is certain, if the members will all pull together and act as an impelling force instead of as a drag on their representatives. The Society has done much in the past, in spite of lukewarm support from many of its members, and more or less open opposition from the outside. The importance of possessing an organisation such as ours has been shown recently in several instances. In short, the Society of Public Analysts, though primarily a scientific society, has other duties to perform, including the guidance of Parliamentary work in connection with the subjects already referred to, and the amendment of the Sale of Food and Drugs Act generally; the discussion of legal points affecting us as public analysts; the assistance of our members in cases in which our common interests are concerned; and in a host of other ways.

#### DISCUSSION.

Dr. SEATON said he thought Mr. Allen's paper was a very valuable and suggestive one as it affected health. The Food and Drugs Act was passed primarily in the interests of health; all the matters touched upon related to health, like colouring-matters, carpets, and so on; and these would seem to be matters that public analysts would be doing good service in reporting upon. Then Mr. Allen had referred to the very important influence they might have in helping to carry out the provisions of the Pharmacy Act. He lately had had to confer with a well-known firm of chemists about a new disinfectant being introduced; it was one that contained a large amount of perchloride of mercury, which, no doubt, could be bought easily, in the same way that vermin-killers could be bought at unauthorised places. There should be some check upon that. Chemists and druggists were bound down by hard and fast rules with regard to the sale of poisons, and other establishments should be watched which are not under the same regulations. The colouring-matter in this case was very distinct, and the remarks which Mr. Allen made with reference to the importance of adopting some colouring-matter which would bear a definite proportion to the poison were, he thought, such as would recommend themselves to others, and of a very practical nature.

Mr. CASSAL said that he thought Mr. Allen's paper was exceedingly important from the point of view of the development of public analysts. Such a development was precisely what was, at the present time, most urgently required; but it would be difficult to obtain without the better instruction and enlightenment of the people who were entrusted with the appointing of public analysts and with the enforcement of the laws against adulteration. Mr. Allen's suggestions did not go quite far enough, but, at any rate, before they could be properly adopted the general state of things at present existing would have to undergo considerable alteration. It would be necessary to teach the public that the sum of 10s. 6d. was not the right measure of the value of an analysis; they would have to endeavour to get that most objectionable clause, which, perhaps, more than anything else, had tended to injure public analysts and to lower their *status*, struck out of the Act of Parliament. There could be no question that a great extension of their duties as public analysts would ultimately come about, but the attainment of this result would not be greatly hastened by discussions in their own body which were not followed by some sort of united action. They wanted additional legislation, or, at least, the extension and amendment of the present laws in the necessary direction. As a matter of fact, every public analyst knew that the majority of local authorities looked upon the "analyst" as a sort of necessary nuisance, who was to be paid the smallest

possible sum for doing the smallest possible number of samples. This was occasionally varied by the payment of the smallest possible sum for the analysis of the largest possible number of samples. It was certainly the duty of the Society to consider as to the best means of improving the position of the public analyst, but the Society was not powerful enough to do what was required. He could not agree that it was even strong enough to afford really adequate support to public analysts in their struggles and difficulties with local authorities. A more powerful body was necessary for this. The extension of their work in the direction of the examination of disinfectants, water, gas, and so forth, was plainly what they were entitled to expect. All such work should be placed in the hands of public analysts, as official chemists. The examination of gas, for example, was at present carried out in the metropolis by a very limited number of "gas-examiners," who were paid an absurdly small remuneration for the work. In the provinces it was practically not carried out at all. It was true that gas was occasionally examined by medical officers of health, and there was the curious fact that these officers also examined water. This led him to another question, that of combined appointments. It would be necessary to put an end to the combined appointments of public analyst and medical officer; it was a thing which led to abuses of all sorts—the farming out of the public analyst's work to a cheap chemist, or of the medical officer's work to a cheap doctor. The holding of combined appointments would have to be strongly discountenanced and, as far as possible, prevented. The subject was one of very wide scope, and he should be glad to hear the opinions of all his colleagues upon it. The future of public analysts largely depended upon their clear appreciation of the position which they held with regard to the public, and the extent to which they might be able to impress the public mind with the enormous importance and the heavy responsibility of their work. A practical suggestion which he would venture to make was this, that every public analyst, whether he was in close contact with his local authority or not, should take every opportunity of instructing that authority upon matters relating to public analysis, with the main view of getting it to work upon the legislature. By united action of this kind all over the country, it was obvious that considerable effects might be produced, which would not only be valuable from a professional point of view, but would be of the greatest service to the public. He suggested that the discussion should be adjourned, so that they could be prepared at a subsequent meeting to enter into a thorough examination of all the points raised.

Mr. DYER said that since the Parliamentary Committee was appointed there had been no occasion to call a meeting; they were not appointed with general instructions to force their opinions upon the legislature, but to deal with definite matters that might arise. While Mr. Cassal was speaking he could not help thinking that that gentleman might have given a little more point to the fact that every rule had its exception. Their worthy President was a public analyst, and was also one of the ablest and most energetic medical officers of health in the country, and after what had happened that evening (referring to Mr. Adams's paper on a new form of air-bath), he (Mr. Dyer) thought they had had a very recent illustration of the practical skill and competence of an analyst in a medical officer.

Mr. CASSAL said that of course he had not had the slightest intention of casting reflections either upon the President or upon Dr. Seaton. He considered that the existence of these combined appointments was injurious to both professions. Among other things, it resulted in this, that the work of one of the two offices was generally not paid for. Certain local authorities got one man to undertake the work of two distinct offices for the pay which should attach to one of them. It therefore appeared to him to be detrimental to the interests of both public analysts and medical officers of

health, that they should hold combined appointments, and he thought the two professions ought to unite in discountenancing them.

After other remarks, and it appearing to be the general opinion of the meeting that the matter should be adjourned, some discussion took place as to the precise terms of the motion, and after various suggestions had been made, it was ultimately resolved, on the proposal of Dr. MUTER, seconded by Dr. JOHNSTONE, "That Mr. Allen's paper be printed and circulated with the agenda for the next meeting, and that the discussion be adjourned until that meeting."

#### RESUMED DISCUSSION ON MR. ALLEN'S PAPER.

The PRESIDENT said that at the last meeting, after a considerable amount of discussion, it was thought better to adjourn it until that evening, and it seemed to him that it might be conducted under three different headings:—

1. Whether it was desirable to promote the wider scope of public analysts duties?
2. If so, could the Society of Public Analysts wisely take any public action in the matter?
3. Whether the present was a good time to take any such action?

MR. HEHNER, before entering into the discussion, read the following extracts from a letter of Dr. A. Ashby:—

"I have received the proof of Mr. Allen's paper. I hope he is not going to agitate for water to be brought within the scope of the Sale of Food and Drugs Act. If it is, we shall not only have an indefinite amount of water analyses forced upon all those public analysts who are paid by fixed salary, but we shall have the general fees for water analysis levelled down to Dr. ———'s fee as advertised in the *British Medical Journal*. I think it is of immense importance that water should be rigidly excluded from the Act; if included we should be laid open to having much work in that direction thrust upon us for nothing, or next to nothing."

MR. HEHNER then said, that the President having laid down for discussion three questions, he should like to see them answered by the Society as follows:—1. It is *not* desirable to extend the duties of public analysts. 2. The Society should *not* take any action in the matter, and 3. The present time is *not* opportune should any action be deemed desirable.

The Sale of Food and Drugs Act comprised all food and drugs used by man; the Act could not well be wider than it was at present, unless all commercial articles were included in it. These were at present satisfactorily dealt with by commercial men interested in them, and by analytical chemists generally, of which division of the profession, public analysts were, after all, but a very small part. Public analysts certainly could not fairly agitate to obtain by law, the work which belonged rightly to the analytical chemists of the country. If they did, they would lay themselves open to the charge of being both needy and hungry, and wanting that which did not belong to them. Were for instance, cattle foods brought within the Act, he had no doubt that those analysts who now controlled the cattle food supply of the country in a most able manner, and to the benefit of the public, would decidedly object to having their work, which they had acquired by their own industry, taken away from them. The same observation applied to petroleum, and many other articles of commerce now analysed by private, not public analysts. As regards water, it was only by the exertion of the Society of Public Analysts that it had been specially excepted from the Sale of Food and Drugs Act, to the benefit of analysts generally.

An unavoidable consequence of widening the Act would be a general depression of fees, which were already now, in most cases, utterly inadequate. This state of things had been brought about by the Sale of Food and Drugs Act. That Act stipulated, that a public analyst should, for a fee of half-a-guinea, analyse any article of food for any private individual. The Act intended, that a salary be paid by the appointing authorities to the analyst, to enable him to do the work for so low a fee. The public, as all were aware, had taken no action whatever, appointing authorities hardly ever did pay salaries, and yet the fee, the official and now generally accepted fee, had been brought down to half-a-guinea for each sample, while formerly two guineas were generally obtained. As a set off the number of samples analysed had certainly much increased. It might be said, that there was no need to mention any fee in the proposed new Act, but he contended, that the half-guinea fee had now become so general, it had become so burnt into the mind of the public, that there could be no hope of obtaining a higher fee, in future. As commercial analyst as well as a public analyst, he therefore objected to any extension of the Food and Drugs Act.

The Society certainly should not take any action. The men who were directly interested in this matter could not well agitate for more work; they would only make themselves ridiculous if they did so. If there were a public agitation, and if to meet a public want a new Act were passed, then of course public analysts would be ready and glad enough to obtain more work.

No time could be more inopportune than the present. Parliament was almost at the end of its natural life, and occupied with other matters. He doubted further, whether any Government, Conservative or Liberal, would risk to make as many enemies as the passing of such an Act would be sure to make. All manufacturing classes would be against it. It should be remembered, that when the Adulteration Act was passed, it roused so much opposition to the then Government, that it was one of the main factors which led to its overthrow. The next Government at once appointed a Committee, and the present Food and Drugs Act was the result. No Government would risk to burn its fingers over such a question again.

He hoped, therefore, that the Society would meet the three questions with a distinct negative. Yet he thought that the subject was one which should be fully discussed by public analysts.

Mr. CASSAL agreed with Mr. Hehner in thinking that the present time was inopportune for taking action, and that it was undesirable for the Society to move in the matter in any official sense, at least at present, but he could not agree with him in the view that an extension of official public analysis was undesirable. He considered that it was desirable in the first place for the benefit of the public, and desirable also for professional reasons and in the interests of both public and private analysts. He could well understand that some members of the profession engaged in commercial analysis should, at first sight, view the extension of official analysis to other articles besides "foods and drugs" with disfavour, but he did not think that they would do so after fuller consideration. The public did not appreciate the value of analytical work. They were ignorant, and could hardly be expected to do so. The inadequate manner in which analysts were paid was largely due to want of proper appreciation of the value of the services rendered, and to a want of proper respect for the professional man who rendered them—in fact, to public ignorance. His belief was that an extension of official work would tend to educate the general public more than anything else. It would gradually show them the great importance of the work, and accordingly would lead to a better appreciation of those who did it. As to the 10s. 6d. fee, he had stated on the last occasion that before any extension of the duties of public analysts was brought about, it would be necessary

to destroy the commonly-accepted and highly-convenient notion that this sum was the proper measure of the value of an analysis. If this could not be done, and if it was to be officially laid down that such a fee was a proper one for any analysis whatever, then he agreed with Mr. Hehner that any extension was very undesirable. But it was necessary to make local authorities and the public, clearly understand the facts about the 10s. 6d. fee. It was a nominal fee, intended to bring the services of an officer in the receipt of a proper salary, and in consideration of such salary, within the reach of persons of moderate means, and at the same time to place some sort of check upon the large class of persons who would willingly make use of the services of a public officer—or of any one else—if they could get them for nothing. It was not intended as a basis upon which the salaries of public analysts were to be calculated, or as a typical fee to be paid to a private analyst. But they (the analysts) had themselves to blame for not uniting together to demonstrate these facts in a practical manner to all those whom it might concern. He was most anxious to see some sort of combination among analysts with respect to their common professional interests. Hitherto they had segregated rather than aggregated in reference to these matters, and had accordingly been taken at a disadvantage. Medical officers of health had succeeded in getting a rather better appreciation of the value of their services than had hitherto been obtained by public analysts. The reasons for this were not far to seek, and it was important that the lesson should not be lost upon analysts. It was through the influence that could be exerted by the public analysts, the only officially recognised chemists, that the profession generally might be benefited. It was a mistake to suppose that an extension of official work would injuriously affect private analysts. On the contrary, it appeared to him to be obvious that the effect of such extension would be entirely the other way. In addition, anything which tended to show how great was the importance of properly conducted analytical work to the community, would plainly be beneficial to the profession, and nothing could accomplish this more satisfactorily than the extension of the work of public analysts, who were in contact with the public and with public authorities, and whose results, in consequence of their position, became public property, and were spread over a wide area. But it was essential that they should be united in resisting all attempts to minimise their position or to detract from the value of their work, whether those attempts were made by individuals or by public bodies. He felt that while the extension of the machinery of the Sale of Food and Drugs Act so as to comprise other articles, would be attended with many difficulties, and would meet with much opposition, it was their duty to take steps when the proper time came, as it probably soon would, to secure the analysis by public analysts of certain articles, the unrestricted sale of which was dangerous to the public health. Among these might be mentioned arsenical pigments, articles of clothing, of decoration, and for other purposes, containing arsenic and other poisons, so-called patent medicines, various quack preparations, “disinfectants,” falsely so-called, and so on. They would not get everything at once, and more attention was likely to be paid to matters involving injury to health. The subject was an extensive one, but he thought that it would be well if the Society could arrive at a decision on the question of the desirability of extending public analysis. He did not think that their taking unofficial action when the time was ripe for it, would have any of the bad consequences which had been anticipated, or that it would be in any way derogatory to their dignity as professional men. It could not be denied, at any rate, that an extension of public analytical work would be a good thing for the public.

Mr. Cassal stated subsequently that he thought he ought to apologise to the Society for having read a paper at Worcester recently upon “The Extension of Public Analysis,” inasmuch as this discussion would have probably led him to modify some of

the views he had expressed in that paper, if he had heard it previously. If he had thought that the sum of 10s. 6d. was likely to be introduced as the measure of the value of an analysis in any Act extending public analysis, he would have burnt his Worcester paper without hesitation. He was very anxious to impress upon the Society that no extension should take place unless the 10s. 6d. fee and the 10s. 6d. spirit were got rid of. He adhered to his original view that the only real way of advancing general professional interests was through the influence which could be brought to bear by the official public analysts. The curses of their profession had been, and still were, a want of mutual confidence and a want of united action. If once they got the importance and responsibility of their work more adequately recognised, great benefits would be derived not only by the analysts in this country, but by the profession in every part of the world.

MR. DAVIES said that it appeared to him that such an extension was eminently desirable, and he did not think private analysts would view it with the feelings indicated by Mr. Hehner. The direction in which he thought that they might advance was more particularly that of official analysis—such analysis and analytical investigations as were directly of use to the public, and brought to the public analyst by the vestry or the authority by whom he was appointed and for whom he was working. It appeared to him that the question of public risk was one that mainly belonged, in no small degree, to the public analyst, who, after all, worked in the interest of the district, as much as the medical officer of health, or the vestry clerk, or the surveyor, and he did not go outside his duties if he endeavoured to bring about a systematic examination of those articles that were largely used by the public, and brought such examinations into line with his ordinary duties as they at present understood them.

The directions that particularly occurred to him then were the analysis of papers and fabrics that might contain arsenic or other deleterious matters, and disinfectants, and what was now done irregularly by some authorities might be done regularly.

Respecting other matters, such as petroleum, he was not by any means sure that it would be an advantage that that article should come under the public analyst's province, and with regard to the Pharmaceutical Society's functions as to passing it did not appear to him that it would be useful to transfer them to the public analysts. As to whether the Society of Public Analysts should take action he agreed with Mr. Cassal and Mr. Hehner that it would be inadvisable for the society to consider such a matter at present. The time was not a proper one, nor was the Society at all in a position to usefully move in the matter.

MR. DYER said that he had had during the day the pleasure of a conversation with Mr. Heisch, who was struck with what seemed to him like a lament on the part of Mr. Allen, that water did not come within the official duties of a public analyst, seeing that it was solely by the anxious persistence of the Society years ago that water was excluded from the Act. As originally drafted the Bill included water, but the Society's then Secretaries, Messrs. Heisch and Wigner, made such representations to those who had charge of the Bill, that the clause was withdrawn; and that was done in the interests of public analysts. As Mr. Heisch pointed out, the public analyst of a district was naturally the man who got the work in his private capacity, and as a rule he got more for it than if his fee was fixed by the Local Board and under the Act of Parliament. With regard to the question of arsenic, there was a bill in existence which had been very carefully drafted, and dealing with it very much on the lines of the Acts of other countries. It had been prepared by the National Health Society, who were awaiting a suitable opportunity to introduce it into Parliament. Care was taken that the official chemist should be the public analyst of the district in which the samples were taken—

wall papers, toys, and so on. Also that the Sale of Food Act should be read as part of that bill as regarded sampling, analysis, and procedure. The bill would be introduced into Parliament at some time or other, but they had been advised that the present moment was inopportune for dealing with the question. Mr. Allen said that Corporations and Boards of Health suffered largely from deficient strength in the carbolic powders supplied to them. Why should they suffer? They were made up generally of business men, and why did they not submit the powders to the analyst and have them analysed? An Act of Parliament was not needed for that as was the case with food and water and milk, or arsenical wall papers where the State might properly step in. But with Corporations and Boards of Health who send out invitations for tenders and have samples and guarantees, why should an Act of Parliament be necessary to enable them to have these things analysed.

Mr. SMETHAM said he was not a public analyst under the Act, and therefore in stating his opinions he did so from an outside point of view. He had listened to what had been said that evening and had come to the conclusion that it would be undesirable, unless some provision could be made to raise the fees, to bring into the Act all these outside substances suggested by Mr. Allen. As Mr. Dyer had pointed out, Corporations and the public at large were pretty well able to take care of themselves as far as the money value of substances was concerned, but not as regarded the wholesomeness of the food they consumed. But the Act was brought into existence more particularly for the protection of the lower classes who were totally unable to guard their own interests, and therefore the State considered it its duty to protect them against the injury to health caused by the fraudulent devices of unscrupulous dealers. The question seemed to resolve itself into what Mr. Allen had called "State Chemists." It was really more a question, if carried to its ultimate limits, of the introduction into England of men who would undertake the whole of the work that might be required from a chemical point of view. He thought that if such men were appointed it would tend in some instances to bribery and fraud. More important still the inspection would hamper the various trades and industries now in existence. Of course, personally, he had no sympathy whatever with fraudulent devices or any adulterations, whether it be soap or what not, but it was certain that the cheaper articles which, as he understood, Mr. Allen would keep a control over, although adulterated were sold as a rule at their relative market prices and the public practically was not cheated. So far as the extension referred only to the protection of health, testing wall papers, etc., then he was certainly in sympathy with Mr. Allen, and the extension he advocates, but when he goes beyond those limits, and seeks to keep a control over ordinary commercial manufactures having no bearing on the public health, he thought Mr. Allen was going beyond the province of the public analyst.

Dr. VIETH said that in his opinion it would not be opportune for the Society to move in the direction suggested by Mr. Allen. Referring to Mr. Cassal's remark, that they should endeavour to impress the authorities on certain points, one point should be the desirability of magistrates imposing heavy fines where adulteration was proved. Another point was for the authorities to direct the inspector where and when he ought to take samples. He had a particular case in view. They all knew they could pretty easily detect the adulteration of milk with water, but it was most difficult to prove to the satisfaction of the magistrate the abstraction of cream. And as long as samples were taken in the streets that would be so, and if a fine were imposed it might be on the wrong man, some poor fellow who could not protect himself. Samples should be taken not only in the streets but at railway stations. It was only two nights ago that forty churns of skim milk were unloaded at one of the termini, evidently intended for mixing with whole milk. He had it on the authority of



an eye witness that a churn of skim milk was divided amongst different churns of whole milk which were not quite full, and, of course, sold as whole milk. If inspectors could take samples at railway stations they would soon put a stop to that sort of thing.

Mr. S. HARVEY said that he felt disposed to give the paper his cordial support, as Mr. Allen had put his finger upon several weak points. He had been somewhat puzzled by the nice distinction drawn by a previous speaker between the advisability of legislation as regards arsenical papers and fabrics, and the non-interference with such articles as soaps and disinfectants. With reference to the latter, it appeared to him that when they were deficient in antiseptic properties they were at least indirectly injurious to health, because they were assumed to possess specific purifying effects, which did not really exist, and that thus the public would be misled. Referring to soaps, he was an observer some years ago of the effects following the introduction of a softened water supply to a borough previously dependent upon very hard well waters, severe eruptions both upon face and hands became, for a time, common, and were attributed to the caustic lime used in the softening process. His observations induced him to regard the use of impure and cheap scented soaps as the real cause. On the other hand he was personally opposed to over-legislation instancing the regulations at present affecting the sale of poisons. An experience of more than thirty years as a pharmacist had convinced him that the public were better protected, so far as chemists were concerned, prior to such legislation, than at present, when so many poisons were really more accessible than they were at the hands of outside dealers. When accidents happened, the latter were seldom, if ever, censured, while chemists were often exposed to most vexatious persecution, even after compliance with all the regulations enforced by the Act.

Mr. E. G. CLAYTON said he thought it would be a mistake from all points of view for the Society to move for this legislation. It would be bad for all parties—for public analysts as well as private analysts. For instance, if water were included at a legalised fee of (say) a guinea, public analysts would be compelled to make these laborious analyses for that sum, and other analysts would have to do the same.

Mr. ADAMS said that with regard to fabrics, wall-papers and perhaps other things there was great room for improvement so far as the public were concerned, but as to other matters he could not agree with Mr. Allen, as others had been unable to agree with him that evening. As to the first point, whether it was desirable to extend the Act, he agreed so far as the substances mentioned were concerned, but whether it was a proper time, or they were the proper body, he had his doubts. Their being only a small body, it would be difficult to persuade the public that they were not acting a self-interested part. All they could do was to stimulate the authorities through members of Parliament and others. With respect to the time, he thought it was very inopportune. The Public Health Act, generally speaking, was not welcomed by the public at large, nor by the public bodies who had to execute the Act against the inclinations of the general public. In witness of that he might appeal to the fact that where public analysts were appointed by small bodies, the analyst got very little work. This meant that the appointing bodies were against the working of the Act, and they only reflected the feeling of their constituencies. It was only by large bodies, unshackled by trade associations, such as county authorities, that the Act was vigorously worked. For that reason he thought they might assume it was unwelcome and would be unacceptable in a Parliament the members of which would have to look about them for popular favour when they went before their constituents. The proposal must not come through their body, but from members whom they could personally influence, and not at a time when Parliament was on the eve of a change. With regard to water, he did not wish to see

it included in the Act, but would very much like the examination of water to be made a local business, for he was positive that no one in England knew better than he himself did as regarded the water in his neighbourhood (Maidstone), and others no doubt were in a position rightfully to say the same for themselves, and from that point of view it would be better that it should be the duty of the public analyst to examine it; but on the other hand he should be ashamed to see the fee reduced to such a ridiculous and totally inadequate sum as 10s. 6d. There were several points which had been raised on which he should have liked to say a few words. One was the National Health Association, and he hoped they might congratulate themselves that it was still in existence, and at all events, and it is to be hoped, in earnest, in bringing forward the question of arsenical poisoning. With regard to disinfectants and soap, he was in sympathy with Mr. Harvey. It was of the greatest importance that the public should be informed of what they used in the dire necessity of an outbreak of fever, although his own experience as medical officer of health led him to place less and less faith in disinfectants.

MR. ALLEN, in reply, said it was not to be expected that everyone would agree with him on all points, but he thought he might safely leave one half of his critics to answer the other half.

He had been misunderstood on one or two points. He never intended to suggest that drinking water ought to be included in the Act. He simply mentioned that it was not included at present. Of course there were some instances where, according to the terms of the appointment, the analyst was expected to undertake analyses of water for Sanitary Authorities in the district for which he acted; but in such cases he believed there was always a special fee allowed. In fact, he was by no means in favour of the 10s. 6d. fee for food analysis, and he thought that one of the very reasons why they should attempt to get an amended act. If an Act were drafted without their having their say in it they might depend upon it the fee would not be amended. He quite agreed that the trouble and responsibility attached to the making of official analyses under the Sale of Food and Drugs Act were by no means remunerated by the fee of 10s. 6d., which had undoubtedly been originally introduced for the purpose of giving private purchasers the opportunity of having the articles they purchased tested at a moderate charge; it being assumed that the analyst would be recouped out of the salary he received from the authorities appointing him.

Mr. Allen could not agree with those who considered that the present time was inopportune so far as Parliament was concerned. The present Parliament, if it lasted its natural life, had still three or four sessions before it. The introduction of a new Sanitary Analysis Act was by no means calculated to bring strong political feelings into conflict, and they might depend upon it that whatever Government introduced a Bill, there would be plenty of cross voting. If the present Government remained in office they had plenty of time before them to pass a Bill as suggested; on the other hand, if their opponents succeeded to power the objection raised did not apply. In either case, therefore, he thought that they should be prepared. He thought they should appoint a Committee who should draft a Bill as carefully as possible and then pigeon-hole it. If when they pressed the matter on members of Parliament with whom they came in contact and were asked, "What do you gentlemen desire?" they would then only have to produce the Bill and say, "This is what we wish." On the other hand, if they did nothing now, the time would come when all would have to be done in a hurry, and we should find that a Bill was drafted and introduced in which our opinions and interests were wholly ignored. He did not agree that it was not possible for public analysts to draft such a Bill. They were undoubtedly the best qualified body of men in

the Kingdom to express an opinion on the point, as they best knew the difficulties of the past and the requirements of the future. He was not inclined to insist that the Act proposed should cover all the articles he mentioned. He thought there was a great deal to be said in favour of making the Act one simply relating to sanitary chemistry, and he should be disposed to leave such things as petroleum and mixed fabrics alone. He could not see that it would in any way have an injurious effect upon the interests of chemists who hold no appointment at present under the Sale of Food and Drugs Act. There were undoubtedly a large number of articles which he suggested should be made the duty of the public analyst to examine, which, at present, were not examined at all. If these were brought within the operation of a future Act it would be sure to bring work to the unofficial analysts, who would be consulted by the manufacturers and dealers in the same manner as they are at present, respecting articles subject to inspection. Whether they took any step or not he must remind them that there was sure to be legislation on the subject of poisons during the next Parliamentary Session.

Respecting disinfecting powders, he certainly considered these should be brought within the operation of the Act, and that the vendors should be compelled to state the strength or composition on the label, so that people would not be buying as carbolic powder, preparations containing merely an insignificant amount of the active ingredient. Similarly with sanitary soaps. It ought to be made illegal for a firm to state that their soap contained certain substances having a curative or emollient action, actually naming those constituents, when, as a matter of fact, there was nothing of the kind present.

With reference to the term State Chemists, which he had used in his paper, he might say that the title did not originate with him, but he believed was due to the President. He had simply adopted it as being, in his opinion, a highly suitable title.

*Conclusion of the Society's Proceedings.*

## THE ELECTROLYTIC SEPARATION OF CADMIUM FROM ZINC.

By EDGAR F. SMITH AND LEE K. FRANKEL.

THE separation of these metals has been effected by Yoer (*Bull. Soc. Chim. de Paris*, 34, 18), who employed the acetates for this purpose.

Eliasberg (*Zeitschrift für Analyt. Chemie.*, 24, 548) and Smith and Knerr (*Am. Chem. Journal*, 8, 210) confirmed this observation, at the same time emphasising the fact that the current should be carefully regulated, otherwise unsatisfactory results would be obtained. A solution containing cadmium and zinc as tartrates, together with free tartaric acid, will also yield all its cadmium to a current generating 0.4—0.5 c.c. oxy-hydrogen gas per minute (*Am. Chem. Journal*, 8, 210). We have no record of other salts of these metals having been used for their electrolytic separation, and therefore taken occasion to learn what might be the result with solutions of the double cyanides, such as we employed in separating mercury and copper (*Journal Franklin Institute*, 127, 386, and *Am. Chem. Journal*, 11, 264).

Beilstein and Jawein (*Ber. d. d. chem. Gesellschaft*, 12, 446, 762) have shown that both cadmium and zinc can be completely precipitated from a cyanide solution, but have not given the current strength employed by them in their experiments, nor did they attempt the separation of these metals from each other.

As our experience with mercury and copper clearly indicates, it is frequently possible by close attention to the current, to effect electrolytic separations, which ordinarily

seem impossible. With this fact clearly before us, our first work with the metals now under consideration was to ascertain how feeble a current would suffice for the complete deposition of each metal, when alone in a cyanide solution, in the presence of an excess of an alkaline cyanide. We very soon discovered that the cadmium separated readily and with a much weaker current than was necessary for the deposition of the zinc. The latter will, however, separate from a cyanide solution, even under the influence of a feeble current, but not until the excess of cyanide has been completely decomposed. With the quantity of cyanide used by us, and with a current of the strength indicated below, this complete decomposition of the alkaline cyanide is not likely to occur in a shorter period than forty-eight hours. Hence, it follows, that as the quantity of cadmium used in our experiments is entirely precipitated in a little more than eighteen hours, the complete separation of cadmium from zinc is thoroughly feasible by this method.

All our experiments were conducted in the cold, and care was taken in each case to examine the deposited metal for zinc, and the residual solution for cadmium. The conditions under which our work was carried on and the results obtained are these—

| Metallic Cadmium in Grammes. | Cadmium found. | Metallic Zinc present. | Difference in per cent. of Cadmium. | KCN in Grammes.                 | Total Dilution. | Current in c.c. of O-H Gas.  | T me.        |
|------------------------------|----------------|------------------------|-------------------------------------|---------------------------------|-----------------|------------------------------|--------------|
|                              |                |                        | Per Cent.                           |                                 |                 |                              |              |
| ·1817                        | ·1813          | ..                     | - ·22                               | 4·5 grammes in each separation. | 200 c.c.        | 0·3 c.c. in each experiment. | 18-23 hours. |
|                              | ·1818          | ..                     | + ·05                               |                                 |                 |                              |              |
|                              | ·1815          | ..                     | - ·11                               |                                 |                 |                              |              |
|                              | ·1822          | ..                     | + ·22                               |                                 |                 |                              |              |
|                              | ·1812          | ·2000                  | - ·27                               |                                 |                 |                              |              |
|                              | ·1818          | ·2000                  | + ·05                               |                                 |                 |                              |              |
|                              | ·1828          | ·2000                  | + ·60                               |                                 |                 |                              |              |
| ·2426                        | ·2422          | ..                     | - ·16                               |                                 |                 |                              |              |
|                              | ·2432          | ..                     | + ·24                               |                                 |                 |                              |              |
|                              | ·2426          | ..                     | ..                                  |                                 |                 |                              |              |
|                              | ·2420          | ·2000                  | - ·24                               |                                 |                 |                              |              |
|                              | ·2435          | ·2000                  | + ·30                               |                                 |                 |                              |              |
|                              | ·2429          | ·2000                  | + ·12                               |                                 |                 |                              |              |
|                              | ·2426          | ·2000                  | ..                                  |                                 |                 |                              |              |
|                              | ·2433          | ·2000                  | + ·28                               |                                 |                 |                              |              |
|                              | ·2434          | ·2000                  | + ·32                               |                                 |                 |                              |              |

The cadmium deposit was light grey in colour and crystalline in structure. It was washed with hot water and dried upon a warm iron plate.

Chemical Laboratory of the Univ. of Pa., Philadelphia, Pa.

## SOME CAUSES OF ERROR IN BLANK ANALYSES.

By J. B. MACKINTOSH.\*

IN making chemical investigations, it is quite usual to run a blank analysis, in order to apply a correction to our results for the impurities contained in the reagents and for those entering into solution from the apparatus used. As a rule however, it seems to be entirely overlooked that the conditions of the actual analysis are often quite different from those obtaining in the case of the blank. For instance, let us assume the case of a limestone which has been dissolved in just sufficient hydrochloric acid to form a neutral solution of calcium chloride; at this stage our blank analysis will be a strongly acid solution. If we now add to both enough ammonia to neutralise the amount of hydrochloric acid previously employed, we will have in our actual analysis a strongly ammoniacal solution, while in our blank there will be a neutral solution of ammonium chloride, and similar results will take place on the addition of every reagent. In such a case our blank analysis will give us only approximately correct results, for though any impurities existing in the chemicals will be detected, yet the impurities which are dissolved from our beakers by the solutions, will be quite different in the case quoted, and the errors due to this last source may far exceed those due to impurities contained in the chemicals used.

The particular case of blank analysis to which I desire to call attention, serves to illustrate the serious error into which chemists may be led by faith in the infallibility of books of reference, whose statements, copied from one another, gain in authority through force of iteration, even though, as sometimes is the case, the original statement be erroneous.

Several years ago I had occasion to analyse a large number of samples of metallic copper and alloys of copper, and for the determination of arsenic I decided to use the method of distillation with ferric chloride and hydrochloric acid recommended in Crooke's *Select Methods*.† In that work the statement is made that the ferric chloride employed may be freed from all traces of arsenic by one or two evaporations to dryness with hydrochloric acid, whereby the arsenic will all be volatilised as chloride. In following these directions I collected the distillates, thus making a blank analysis in all respects similar to the actual analyses performed later. When the distillates were tested for arsenic they were found to be perfectly free from that element, from whence the deduction was drawn that the reagents employed were pure. If the statement mentioned above was correct, then this deduction was justified by the facts observed. I noticed, however, that all the samples of copper I had, no matter of what quality, invariably caused the appearance of large quantities of arsenic in the distillates, and on repeating the experiment with the substitution of some charcoal for the copper, I likewise obtained arsenic in the distillate, and since the charcoal could not be suspected of being the source of the arsenic found, it was definitely traced to the ferric chloride, which by a blank analysis would have been pronounced pure. In this case the omission of the copper in the blank

\* *Journal of Analytical Chemistry*.

† First Edition, p. 266; Second Edition, p. 431.

analysis was also the omission of a necessary reagent, without which or some substitute, the reaction would not take place. In fact, it is not until the arsenic is reduced to arsenious chloride that it will distil off, any arsenic in the higher form of oxidation not being volatile under these circumstances.

Here is a striking instance of the unreliability of blank analyses, unless all the circumstances be thoroughly comprehended and taken into account, and other instances of similar nature could readily be adduced.

### REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

USE OF OXYGEN IN QUANTITATIVE ANALYSIS. W. MINOR. (*Zeitschr. f. angew. Chemie*, No. 23, 1889).—It seems strange so little use is made of oxygen in technical laboratories. Take for instance wine analyses, where the getting of a proper ash, without volatilising chlorides, is a difficult operation. If, however, the extract is heated in a current of oxygen, the ash is got ready in a few minutes. Another instance is furnished by cane-sugar and allied bodies. Although this is generally first moistened with sulphuric acid and the weight of the ash multiplied by  $\cdot 9$ , still the treatment in oxygen will dispense with the use of the acid. In the estimation of carbon in pig-iron, the use of oxygen is very advantageous. The iron is placed in solution of cupric chloride, which gradually dissolves the iron, leaving an impure carbon. This is collected on an asbestos filter dried in a platinum crucible at  $120^{\circ}$  C. and weighed. The carbon is then burnt in oxygen and found from the loss in weight. Oxygen will also be found advantageous in the estimation of sulphur or sulphates. The well-washed precipitate of barium sulphate is put moist in a platinum crucible, and after charring ignited in a current of oxygen. This will prevent all chance of reduction, and the operation is done in a few minutes.

L. de K.

BORGMAN'S PROCESS FOR THE ESTIMATION OF THE ACIDS IN WINE. R. GANS. (*Zeitschr. f. angew. Chemie*, No. 23, 1889).—This process, consisting in treating the wine extract with alcohol, to precipitate the cream of tartar and dissolve out the free acids, has been found by the author to yield uncertain results. As the results of his experiments he concludes:—1. The estimation of the cream of tartar is influenced by the amount of sugar. If much sugar is present some of the cream of tartar does not separate out, and some free tartaric acid remains undissolved. 2. The estimation of the free tartaric acid (by means of potash) is also inaccurate, as especially in absence of sufficient sugar nearly the whole of the acid potassic malate also separates out. In fact, the process can only be trusted to give approximate results in the case of very sweet wines.

L. de K.

DETECTION OF SMALL QUANTITIES OF NITROUS ACID. G. LUNGE. (*Zeitschr. f. angew. Chemie*, No. 23, 1889).—A well-known disadvantage of the otherwise so excellent reagent of Griess for nitrous acid, is the circumstance of the solution, even of the whitest looking (*a*) naphthylamin, getting dark and therefore losing in sensitiveness. When the solution to be tested is very dilute (1-1,000000000), the test works so slow,

that one cannot be certain whether the nitrous acid has not been absorbed from the atmosphere. Even after warming, which facilitates the reaction, the test may not show for 15 or 20 minutes. Jlosvay shows that by using acetic instead of sulphuric or hydrochloric acid the reaction takes far less time, and the colour is also intensified. He also states that the darkening of the reagent may be prevented by boiling some solid naphthylamin with water, and only using the fluid which has been poured off from the residue. In fact, he gives the following recipe:—1. Dissolve .5 gramme of sulphanilic acid in 150 c.c. of dilute acetic acid. 2. Boil .1 gramme of solid (*a*) naphthylamin with 20 c.c. of water, pour off from the blueish deposit, and mix with 180 c.c. of dilute acetic acid. The liquid to be examined (about 20 c.c.) is mixed with a few c.c. of the sulphanilic acid, warmed till about 80° C., and then mixed with the solution of the naphthylamin. Even when the solution contains only one thousand of a millionth part of nitrous acid, the red colour will appear after one minute. If the proportion of the nitrous acid is larger, say 1 in 1000, only a yellow colour will appear, unless a large quantity of naphthylamin is added. The author on the whole agrees with Jlosvay, only thinks he can still further improve it. The test for nitrous acid is just as delicate and quick, if two reagents are mixed and kept in a well-stoppered bottle. Air must be as much as possible excluded, but it is not necessary to keep the reagents in the dark. By this small modification we get the great advantage of using *one* solution only. Then if the two solutions are kept separate, one can never tell whether perhaps one of them has absorbed a little nitrous acid from the air. If, however, the mixed solution should absorb any nitrous fume, it would at once betray this by the reddish colour. If a solution should have got coloured, it is often possible to restore it to its original condition by shaking it with zinc dust and filtering.

L. DE K.

ESTIMATION OF IRON AND ALUMINA IN PHOSPHATES. E. GLASER. (*Zeitschr. f. angew. Chemie*, No. 22, 1889.)—The process for the estimation of iron and alumina in phosphates, as now practised, is not applicable to any variety of phosphate, and therefore not very useful. Its shortcomings have shown themselves more particularly in the last few years, when many samples of Belgian and similar phosphates are on the market. The results are somewhat dependent on the amount of acetic acid used, then aluminic phosphate is somewhat soluble in excess. This conventional process is as follows: The precipitate insoluble in acetic acid is filtered off, washed with cold water, and then dissolved off the filter with hydrochloric acid. After adding a little microcosmic salt the liquid is rendered alkaline with ammonia and then mixed with acetic acid. The precipitate is washed, dried, and ignited, and half of its weight is called iron and alumina. No wonder analysts differ in their results from 1 to 3 per cent. Not only, however, is the error solely due to the slight solubility in acetic acid, but also to the fact that in the original sample, the iron is not always in combination with phosphoric acid. When such a solution is precipitated with ammonia, the lime and magnesia are precipitated as phosphates, which is also the case with the iron and alumina, if there is a sufficiency of phosphoric acid. This, however, is not always so, and then there forms a precipitate of ferric and aluminic hydrate, which redissolves in excess of acetic acid and so get lost.

Then again the ferric acetate has a solvent action on ferric phosphate. If too little acetic acid is used the precipitate may contain lime and the result is equally faulty.

(Note by abstractor: Iron and alumina phosphates will not properly come down with ammonia and acetic acid if the phosphate contains organic matter, which is very often the case. This being absent, all iron and alumina will certainly come down, except in cases where there is a want of phosphoric acid).

The author now tried to find a process which will dispense with the acetic acid, and succeeded by the use of alcohol as follows: 5 grammes of phosphate are dissolved as usual in 25 c.c. of nitric acid of 1.2 sp. gr., and 12.5 c.c. of hydrochloric acid, and diluted up to 500 c.c. 100 c.c. of filtrate (= 1 gm. sample) are put into a 250 c.c. measure and mixed with 25 c.c. of strong sulphuric acid. After standing for about five minutes and occasional shaking, 100 c.c. of alcohol are added, and the whole well shaken. After cooling alcohol is added up to the mark, but as there is always a little contraction it will be found necessary to later on add some more spirit. After at least standing for half an hour the liquid is filtered, and 100 c.c. (= .4 gm. sample) are evaporated in a platinum dish till alcohol is expelled. The acid fluid is rinsed into a beaker with about 50 c.c. of water, and heated to boiling. After cooling a little ammonia is added to alkaline reaction, and if necessary the excess of ammonia is expelled by boiling. The precipitate is now collected, well washed, dried, and ignited. It consists of pure ferric phosphate and pure aluminic phosphate. The iron phosphate can be determined by a volumetric estimation, say with permanganate.

The test analyses given are very satisfactory, more so than the analyses performed by the conventional process.

L. de K.

DETECTION OF GROUND-NUT OIL IN COD-LIVER OIL. V. BISHOP. *Journ. de ph., et de chim.*, xx. p. 302.—Ground-nut oil is frequently added to cod-liver oil with a double object, viz., to give to the Cod-liver oil a more pleasant taste and to increase the profits of the vendor. It is therefore to our great interest to be able to detect it, and seeing that it does not possess characteristic properties, as does, for instance, oil of sesame, its detection is very delicate and uncertain. Nevertheless, having studied the question the author believes it to be quite possible to arrive at a satisfactory solution. The colouration furnished by acids—notably by sulphuric acid, the estimation of the iodine, etc., do not always give exact indications. The density, the heating power of the sulphuric acid, the absorption of bromine are three modes of analysis capable of giving much more exact results, on account of the notable differences which exist in these respects between the two oils.

To reply, then, the author works in the following manner:—

1st. The density is taken by the areothermic balance with the usual precautions.

2nd. The action of sulphuric acid on cod-liver oil and even on ground-nut oil being very energetic, and producing a strong disengagement of sulphurous acid, it is indispensable to mix them with a known quantity of a retarding oil, the heating power of which is at once low and ascertained. With this object the author employs heavy mineral oil, which, as is well known, possesses a very low point of heating power, with sulphuric acid, and such oil he mixes with the cod-liver-oil in equal proportions.

3rd. In applying the bromine absorption method, the author employs M. Halphen's process, by which the oil is saponified and the fatty acids liberated in the usual manner. 1 c.c. of these acids having been dissolved in 20 c.c. of carbon bisulphide, the solution is treated with a fixed excess of a standardised solution of bromine.



After standing the usual time, the unabsorbed bromine is estimated by a standard solution of soda, strongly coloured with cosine. On applying these methods to standard samples, the author has obtained the following results :—

|                         | Density to 15°. | Heating power with<br>sulphuric acid 10 gr. oil.<br>10 gr. of mineral oil.<br>20 gr. of sulph. acid. | True heating<br>power. | Absorption<br>of<br>bromine. |
|-------------------------|-----------------|--|------------------------|------------------------------|
| White cod-liver-oil     | .. 0.9265       | 67°  | 106°                   | 0.732                        |
| Light " "               | .. 0.9257       | 65°  | 102°                   | "                            |
| Brown " "               | .. 0.9264       | 65°.25   | 102°.5                 | "                            |
| Ground-nut oil          | .. 0.917        | 48°  | 66°                    | 0.534                        |
| Mixture, 21% ground-nut | } 0.9243        | 62°.5  | 97°                    | "                            |
| " 80 % white oil        |                 |  |                        |                              |
| Mineral oil             | .. 0.9243       | 14°  | 97°                    | "                            |

M. S. A. M.

### REVIEWS.

AN INTRODUCTION TO CHEMICAL SCIENCE. BY R. P. WILLIAMS, A.M., INSTRUCTOR IN CHEMISTRY, ENGLISH HIGH SCHOOL, BOSTON, U.S.A. EDITED AND REVISED BY B. P. LASCELLES, M.A., F.C.S., ASSISTANT MASTER AND LIBRARIAN, HARROW SCHOOL. LONDON: GINN AND COMPANY.

THIS is decidedly the best practical book we have yet seen for use in schools. It is essentially an elementary book, and is not written with the view of examination, but is formed on a specially interesting plan leading the learner through a series of experiments which convey to him a very fair idea of the chemistry of common things. Commencing with weights and measures and passing through a short account of what chemistry is, and of atoms, molecules, etc., the authors go first through the non-metals, then take up some of the chief industrial metals, and finally indulge in a little dip into organic chemistry, mentioning such matters as gas-making, fermentation, soap manufacture, etc. A boy working through the book in a school laboratory would acquire exactly what a schoolboy should, viz., a good groundwork enabling him to have ideas as to the composition of the articles he sees around him, and of the chief industrial chemical processes. It is true that he would not be specifically prepared for any particular examination, but he certainly would have much broader views than boys that are so taught, and we should say that he would pass the College of Preceptors or any such preliminary very easily in the subject of chemistry. Every schoolmaster who has a laboratory should get a copy of this book and let his boys use it if he wants them to be really interested in the study of chemistry. It is printed in good, bold, readable type, and extends to 223 pages, 8vo. size, at the moderate price of 3s. 6d.

### CORRESPONDENCE.

[The Editor is not in any way responsible for opinions expressed by his correspondents.]

To the Editor of the ANALYST.

SIR,—In reference to the communication from Mr. Percy Smith in the November number of THE ANALYST, we desire to say that, while it might appear to any one reading the review of our "Water Analysis" in the preceding number, that we had adopted, without credit, the explicit descriptions given by Mr. Smith, yet, as a matter of fact, due credit is given in the preface to the work. The reviewer, by inadvertence, omitted to note this fact. Analysts are certainly under obligations to Mr. Smith for having demonstrated the trustworthiness of these methods, and furnished clear and practical descriptions for their employment.—Yours,

HENRY LEFFMANN.  
WILLIAM BEAM,

715, Walnut Street, Philadelphia,  
November 22nd, 1889.

# THE ANALYST.

FEBRUARY, 1890.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE Annual Meeting of the Society was held on the 8th ult., at Burlington House, the President, Mr. Allen, in the chair.

The minutes of the previous meeting were read and confirmed.

The Treasurer, Mr. Heaton, read the Auditor's report, showing a balance of £161 in the bank, besides the £100 already invested in Consols.

Dr. Muter thereupon moved, and Mr. Harvey seconded, that the accounts be passed as read, and that a further sum of £100 be invested in Consols.

This was carried unanimously, and the Auditor's report will be circulated amongst the members as usual.

The President then delivered his annual address as follows:—

GENTLEMEN,—My first duty is to thank you most cordially for the support and consideration shown me during my year of office as your President, and I beg you to believe that it has always been to me an honour to be reckoned one of, and far more for the nonce to be the representative, of a body of men who deserve to rank as high as any among the day-labourers in the field of science; for may we not justly claim, without presumption, that during the period of the existence of this Society our labour has been as toilsome, as responsible, and as honourable as any to be found.

*For toil* I see no prospect of abatement. Year by year, as knowledge ripens, the processes we employ become more and more exacting of skill and attention, without, by-the-bye, any increase of remuneration.

*For responsibility*, it is a question if any calling within the domain of applied science throws more burden upon its followers than that of the public analyst, from whom it is

required in the exercise of his never too popular function, to explore regions beset by enemies and pitfalls, without a chart, without a guide, with nothing, in fact, but a sense of duty to keep him to his task.

It is, therefore, all the more *honourable* to public analysts that these difficulties have been so courageously met, and, in large measure, overcome; the credit of conquest falling chiefly to past or present members of this Society.

In pursuit of these ends we have during the past year held eight general and an equal number of Council meetings. At these meetings twenty-three papers have been read; the attendances have been above the average, and the discussions well sustained.

The following is a list of the contributions:—

| PAPERS IN 1889. |  | Author.                          |
|-----------------|--|----------------------------------|
| Date.           |  |                                  |
| Jan. 9.         | "Remarks on a Recent Case of Alleged Injurious Pollution of the River Medway by the Sewage of Maidstone" .. .. . | Dr. Dupré                        |
| "               | "On the Analysis of Pepper and the occurrence of Piperidine therein" .. .. .                                     | Dr. W. Johnstone                 |
| "               | "On the Westphal Balance" .. .. .  | W. F. K. Stock                   |
| Feb. 13.        | "On the Composition of Milk and Milk Products" .. .. .   | Dr. Vieth                        |
| "               | "An Improved Method for the Analysis of Fats" .. .. .  | { Dr. Muter and<br>L. de Koningh |
| "               | "Note on Phytosterin" .. .. .  | O. Hehner                        |
| "               | "On Density" .. .. .   | H. D. Richmond                   |
| March 13.       | "Notes on Lactose" .. .. .   | E. W. T. Jones                   |
| "               | "Colouring Matter (Arsenical) used for Colouring Candles" .. .. .  | W. F. Lowe                       |
| "               | "The Methods for Determining Fat in Milk" .. .. .  | Dr. Vieth                        |
| April 10.       | "Contributions to the Study of the Action of Water on Lead Pipes" .. .. .  | A. H. Allen                      |
| "               | "Iodine Absorption of Butter Fat" .. .. .  | Rowland Williams                 |
| "               | "'Pure' Chemicals" .. .. .   | Bertram Blount                   |
| "               | "Some Experiments on the Soap Test" .. .. .  | Dr. E. Waller                    |
| May 8.          | "On the Discrimination of the Various Species of Saccharomycetes" .. .. .  | Dr. W. J. Sykes                  |
| "               | "Fat Extraction from Milk Solids" .. .. .  | H. D. Richmond                   |
| June 12.        | "On Condensed Milk" .. .. .  | H. Faber                         |
| "               | "On the Quantity of Volatile Acids present in Butter Fat" .. .. .  | Dr. Vieth                        |
| "               | "On the Amount of Volatile Acids in Butter Substitutes" .. .. .  | O. Hehner                        |
| Nov. 13.        | "A New Form of Air-Bath" .. .. .   | M. A. Adams                      |
| "               | "The Possible Future Extension of the Duties of Public Analysts" .. .. .   | A. H. Allen                      |
| "               | "On some Applications of Centrifugal Action in Laboratory Work" .. .. .  | { Dr. H. Leffmann<br>and W. Bean |
| Dec. 11.        | "Adjourned Discussion on Mr. Allen's Paper on the Duties of Public Analysts" .. .. .                             |                                  |

Milk, butter, and fats continue to attract a large share of attention, nine out of the twenty-three papers being devoted to one or the other of these subjects. The contribution of Dr. Muter and Mr. L. de Koningh in February, on "An Improved Method for the Analysis of Fats," gave hope that the year might bring forth some welcome addition to the pressing want of better knowledge of the constitution of, and a means of discrimination between fats, this paper, confessedly an introduction only to a consideration of this important subject, was to be followed by other contributions from the same gentlemen on the application of their process to the analysis of solid fats used for food. I am sure we all regret that as yet Dr. Muter and his co-worker have not been able to redeem a promise which seemed to open out the hope of a new channel for the investigation of the proximate constitution of fats; and the more so, seeing that the work of the Committee appointed by the Society at the end of last year to investigate the subject has been entirely barren of results. But it must not, on this account, be considered that our knowledge concerning the analysis of fats has stood still; far from it. The rays of light that have already been shed upon the subject are being gathered more and

more to a focus by the labour of a host of experimenters ; and in this manner the work, being consolidated into a body of experience of the methods of analysis already to hand, is a result in itself to be counted an important gain, and which, it is to be hoped, may form the basis for the acquisition of additional knowledge in the future.

The papers by Mr. Hehner, Mr. A. Williams, and Dr. Vieth have been full of valuable material of this description.

A paper by Mr. Allen, at the November meeting, on "The possible future extension of the duties of public analysts," was full of interest, and gave rise to a long and animated discussion, the mention of which affords me the opportunity for expressing a hope that when fresh legislation is about to take place the opportunity may be secured for pressing upon the legislature the great need of providing some system for the fixing of officially authorised limits, that shall be fair to traders, fair to the public, and binding on the part of analysts and the official referee. Something of this sort becomes more and more urgently necessary as accumulated experience tends to widen the range of natural variation that we find to occur in the constitution of some natural products, milk and butter to wit, this range of variation being so great as to cover, to all intents and purposes, habitual adulteration to a very large extent.

As things now stand, the trader, the public, the analyst, and the referee, all, indeed, but the adulterator, suffer for want of some system of this sort. The honest trader knows that dishonesty, so long as it is kept within scientific limits, will enable a neighbour to undersell him with impunity ; the public, in proportion as this is possible, are unprotected. The analyst, in the dilemma between duty and self-interest, treads a path often as uncertain as shifting sand, and the official referee, however competent, however just, must at times be sorely puzzled where to draw a line that shall be just between all parties.

It may fairly be argued that in some cases, owing to this natural variation of composition, it is difficult to fix a limit ; just so, that is only too true, and is the strongest possible argument in favour of a limit being fixed. The difficulty has to be faced in any case, and in the present state of affairs this difficulty has to be dealt with over and over again, instead of once for all, by each and every analyst up and down the country wherever the difficulty arises, according to his own light, as best he may, and thereby the burden of the difficulty is enormously extended, and in practice the duty is discharged in an uncertain, and not always in the most satisfactory manner.

Time was when the course I am advocating was impracticable. We need only look as far back as the time of the inauguration of this Society to find universal ignorance regarding the natural variations of composition of such articles as milk, butter, and lard. At that time it would have been unwise, if not impossible, to fix any limits, but nowadays such ground for objection no longer exists, by the vast accumulation of knowledge appertaining to these matters arising out of the work of public analysts, and in large measure contributed by the past and present members of this Society, it would be a comparative'y safe and easy matter to determine what ought to be considered just and reasonable limits for those and other articles.

So far as the present argument is concerned, it is not a question who shall fix the limits, nor whether they shall be high or low, permanent or provisional. As practical men, as working analysts, our chief concern is to have authoritative limits of one kind or another, plain, open, and above board, to work to. If I am not mistaken, we shall all be of one mind as to this, and I think you will also agree with me that it would not be unreasonable that for some things such limits need only be provisional, and subject to review as from time to time the development of the principles and practice of analysis make alterations or modifications desirable ; but as this is matter for the future, and, very likely, not the very near future, a discussion of the details may well be left until

there is more immediate prospect for useful action. Remember it was Mr. Allen's paper that brought the subject of future legislation and the particular interest of our Society in connection therewith to the front, and we may now pass to other matters having more present importance for us.

I have to record that our roll-call comprises the following :

|                  |    |    |    |     |
|------------------|----|----|----|-----|
| Honorary Members | .. | .. | .. | 9   |
| Ordinary Members | .. | .. | .. | 163 |
| Associates ..    | .. | .. | .. | 27  |
| Total            |    |    |    | 199 |

During the year we have been deprived by death of perhaps our most illustrious, and certainly most venerable member, Monsieur Michael E. Chevreul, F.R.S., at the surprising age of one hundred and two years.

Two other members are lost to us by the same cause, viz., Mr. Herbert L. Buckenridge, F.C.S., of London, and Mr. J. W. Montgomery, F.C.S., of Whitehaven, Cumberland, and there have likewise been three resignations.

On the other hand, our ranks have been recruited by the election of seven members and three new associates, so that numerically we have a balance of four to the good.

By the resignation of Mr. Frederick Low, our Honorary Solicitor, caused by his approaching call to the Bar, our Society has sustained a distinct loss. Mr. Low is a very able lawyer and excellent advocate, and during the early part of the year rendered successful service in the interest of one of our most respected members, and through him the Society as a whole, in a case involving an important matter of principle respecting the duties and tenure of office of a public analyst.

I am fortunately in a position also to record that, as regards our finances, we have an increasing balance to our credit of some £63 ; in fact, in all material concerns, we are in a prosperous condition.

The President moved a vote of thanks to the President and Council of the Chemical Society for the use of the rooms during the past year and it was carried unanimously.

The following paper was read and discussed :—"A Rapid Method of Estimating Quinine in Medicine." By Dr. Seaton and Mr. Richmond.

Mr. Allen proposed, Dr. Muter seconded, and Mr. Cassal supported a vote of thanks to the President for his address, and it was carried unanimously.

The Scrutineers, having opened the ballot papers, reported that the following were elected as President and Council for the current year :—

*President*.—M. A. Adams, F.R.C.S.

*Vice-Presidents* (who have filled the office of President).—A. H. Allen ; A. Dupré, Ph.D., F.R.S. ; C. Heisch ; Alfred Hill, M.D. ; J. Muter, Ph.D., M.A., F.R.S.E. ; (Who have not filled the office of President).—Sir Chas. Cameron, M.D. ; T. Stevenson, M.D., F.R.C.P. ; W. J. Sykes, M.D.

*Treasurer*.—C. W. Heaton.

*Hon. Secretaries*.—Bernard Dyer, B.Sc. ; Otto Hehner.

*Other Members of Council.*—S. Harvey ; G. H. Ogston ; Boverton Redwood, F.R.S.E. ; E. Seaton, M.D., F.R.C.P. ; E. W. Voelcker.

The names of those Members of Council whose term of office has not yet expired, and who consequently do not retire this year, are C. E. Cassal ; R. H. Davies ; W. Fox ; R. H. Harland ; W. Sedgwick Saunders, M.D. ; P. Vieth, Ph.D. ; and C. R. Alder Wright, D.Sc., F.R.S.

The following gentlemen were also elected as Members of the Society :—W. Newton, Ph.D., London ; G. H. Masson, Trinidad.

The next meeting of the Society will be held at Burlington House, on Wednesday, the 12th inst., at 8 o'clock.

### NOTE ON SOME APPLICATIONS OF CENTRIFUGAL ACTION TO LABORATORY WORK.

BY HENRY LEFFMAN AND WILLIAM BEAM.

*(Read at Meeting, November 1889.)*

THE efficiency of centrifugal machinery in various separations has been long known, and finds many applications on the large scale. Special uses in analytical work for examination of milk and the drying of precipitates have recently been brought to notice. In connection with experiments on a small machine, modelled after the lactocrite, and intended for use by creameries, we had occasion to note that the principle could be advantageously extended to many laboratory manipulations. The first experiment was made on a sample of slightly turbid urine, with a view of obtaining the suspended matter for microscopic examination. This requires several hours usually, by the ordinary method of subsidence, but we found that a rotation of about one minute, at a speed of 16 revolutions per second, produced a clear liquid, with the entire suspended matter closely packed at the bottom of the tube, this condition permitting the decanting of almost the whole of the liquid without disturbing the deposit. Similar separations were obtained with recently precipitated barium sulphate, calcium oxalate, and Prussian blue. A sample of powdered cocoa, adulterated with starch, on being diffused through water and placed in the tube, showed, after a short rotation, a marked separation of the starch, which appeared as a white stratum in the mass of settled material. We have also found that in extraction by immiscible solvents the separation of the solvent can be rapidly and thoroughly attained. Thus the obstinate emulsion which chloroform sometimes produces with aqueous liquids is at once separated.

The essential feature of the machine we used is that the tube carriers are connected by a hinge to a vertical, revolving rod. This permits the tube to hang upright when at rest, taking a horizontal position only when in rapid rotation. It is, therefore, not necessary to close the tubes with a stopper.

The machine used in the above experiments carried eight narrow tubes, about twelve centimetres in length, and holding but six c.c. These being too small for regular laboratory work, we are having a machine built to carry tubes of much larger size, and we hope soon to describe it in detail, and many applications of it.

*(Conclusion of the Society's Proceedings.)*

## THE ANALYSIS OF BAKING POWDER.

By C. A. CRAMPTON, ASSISTANT CHEMIST U.S. DEPARTMENT OF AGRICULTURE.\*

BAKING-POWDERS may be conveniently classified according to the nature of the acid constituent they contain. Three principal kinds may be recognized as follows:

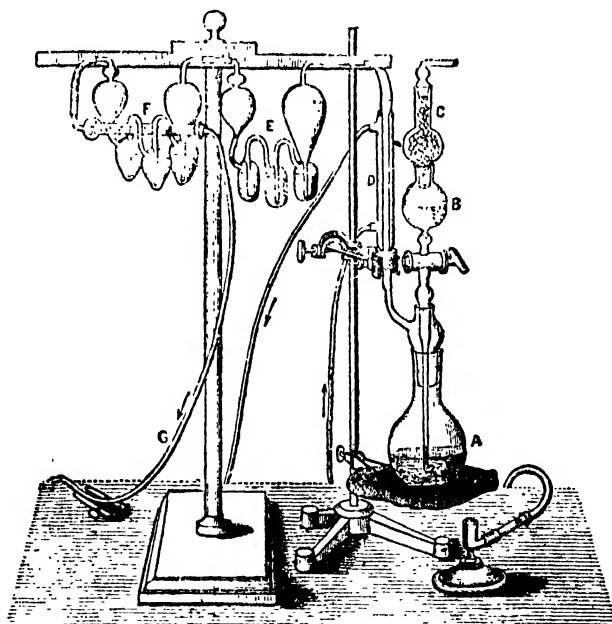
- (1) Tartrate powders, in which the acid constituent is tartaric acid in some form.
- (2) Phosphate powders, in which the acid constituent is phosphoric acid.
- (3) Alum powders, in which the acid constituent is furnished by the sulphuric acid contained in some form of alum salt.

All powders sold at present will come under some one of these heads, although there are many powders which are mixtures of at least two different classes.

The qualitative examination and assignment of a sample to one of the above classes presents no special difficulties. The microscope settles the filling used, but this is usually unimportant. A determination of the alkalinity of the watery solution of the powder is useful as showing whether any great excess of alkali has been used.

## ESTIMATION OF CARBONIC ACID.

This is one of the most important estimations, as it determines the strength of the powder. It was made by absorption with soda lime, and a form of apparatus was used that has served for some time in this laboratory for the determination of carbonic acid.



This apparatus has recently been somewhat modified and greatly improved in compactness by Mr. A. E. Knorr. It is shown in the accompanying figure. The following is Mr. Knorr's description:—

The apparatus proper, as represented by the cut, consists of a flask A in which the carbon dioxide is set free. A condenser D is ground into the neck of this flask and condenses the steam formed when the liquid in A is boiled in order to secure complete expulsion of the gas. The reservoir B contains

\* Bulletin of Department, No. 13.

the acid required for the operation, and has a soda-lime guard C ground into it to retain the carbonic acid of the air, a constant current of which is aspirated through G during the whole operation. The stem of the reservoir is ground into the condenser, or it may be conveniently blown into one piece with it. The carbonic acid is dried in E and finally absorbed in the weighed potash bulb F.

Two determinations of carbonic acid were made on each sample—one by the addition of acid to determine the total amount of carbonate present, and one by the addition of water only. The per cent. of carbonic acid found in the latter estimation may properly be termed the *available* amount present in the powder, as it is the quantity which would be actually liberated by the acid ingredient of the powder when it is used in baking, and therefore represents the actual *value* of the powder for aerating purposes, so far as the *evolution* of gas is concerned.

For the determination of the *total*  $\text{CO}_2$  the procedure was as follows: Place in a short glass tube, the weight of which is known, about 1 to 2 grams. of the sample, and weigh the whole as quickly as possible, the amount taken being obtained by difference. The tube and contents are gently dropped into the generating flask of the apparatus, which must be perfectly dry. The flask is closed with the stopper carrying the tube connecting with the absorption apparatus, and also the funnel tube, which has been previously provided with 10 cubic centimeters of dilute sulphuric acid for the liberation of the gas. When all parts of the apparatus are connected, and seem to be tight, the stopper of the funnel tube is opened, and the acid allowed to run slowly into the flask. The generation of the gas should be made as gradual as possible; by running in a small quantity of the acid at first and tilting the flask slightly this can readily be accomplished; after the greater part of the sample has been acted upon by the acid and before the latter has all been added, a lamp is placed under it, and the contents gradually heated to boiling, gentle aspiration being made at the same time. The operation is finally finished by the funnel tube being opened, and air, free from  $\text{CO}_2$ , drawn through it and through the apparatus, the contents of the flask at the same time being kept at ebullition. This is continued for fifteen minutes, when the absorption tube is removed from the apparatus, allowed to cool, and weighed. Its increase in weight gives the amount of  $\text{CO}_2$  absorbed. The determination of the *available*  $\text{CO}_2$  was conducted in a similar manner, with the substitution of pure boiled water in the funnel tube instead of acid. After the sample has all been acted on, the contents of the flask are just brought to a boil, then the lamp is removed and air is drawn through the liquid for exactly fifteen minutes. The conditions were made as nearly alike as possible for each sample in this estimation, for, different results can readily be obtained by varying them. The above conditions are believed to be as close an approximation to those actually obtaining in the use of the powder as can be arrived at in an ordinary chemical analysis. Prolonged boiling of the liquid residue is inadvisable, for in case the ingredients in the powder are not accurately proportioned, and a considerable excess of bicarbonate is present, long boiling will liberate gas from it after the acid ingredient has all been neutralized, and thus a high result is obtained from a poorly-made sample, while in one where the bicarbonate is not greatly in excess of the proper amount, the above procedure will readily give the full amount available.\*

\*In some experiments made to determine the amount of carbonic acid driven off from bicarbonate of soda on heating its water solution, the following results were obtained: (1) Just brought to a boil under the same conditions as in the determinations made above, 6.99 per cent. of the weight of the bicarbonate was obtained; (2) Boiled 15 minutes, 16.17 per cent. was obtained; and, (3) boiled in 1½ hours, 20.70 per cent., or about the full quantity of acid carbonate.



## ESTIMATION OF STARCH.

This estimation was made by the well-known method of conversion by heating with acid and the determination of the copper oxide reducing power of the resultant solution. While by no means satisfactory, this is probably the best method we have at present for starch estimation. No difficulty was found in its application to all classes of baking-powders, the other ingredients offering no obstacle to its proper performance. To insure agreeing results it is very essential to conduct the conversion under precisely the same conditions in all cases.

The following is the detailed procedure :

From 2 to 5 grams. are weighed out and transferred to an Erlenmeyer flask ; to it are added about 150 to 200 cubic centimeters of a solution of hydrochloric acid which has a strength of 4 per cent. of the acid gas. The flask is provided with a cork, perforated for the passage of a condensing tube about 1 meter in length. The conversion is accomplished by gently boiling the acid liquid for four hours, after which the flask and contents are cooled, neutralized by the addition of sodium hydrate, made up to a definite volume and the copper oxide reducing power determined. The latter operation is best carried out by the method used in this laboratory, in which asbestos-tipped filtering tubes are used for the end reaction.\* The reducing power being calculated as dextrose ; 10 parts equal to 9 parts of anhydrous starch.

Professor Weber used a rough method for the direct estimation of starch in his samples, which he describes as follows :†

One gram. was weighed off, transferred to a small beaker, covered with water, allowed to stand until action had ceased, filtered and washed, residue spurted by means of a wash-bottle into a flat-bottomed platinum dish, allowed to settle, the supernatant water removed as far as possible by means of a pipette, the remainder of water evaporated, the residue dried at 100° C. and weighed. The residue was then incinerated and the amount of ash deducted from above weight. In case of alum powders the ash remaining after ignition was  $\text{Al}_2\text{O}_3$ , which was contained in the residue dried at 100° C. as  $\text{Al}_2(\text{OH})_6$  ; consequently the  $\text{Al}_2\text{O}_3$  was calculated as  $\text{Al}_2(\text{OH})_6$  before deducting.

This method was carried out upon the entire series of samples examined here. In many cases it gave results agreeing quite closely with those obtained by the direct estimation, but in some samples the results were entirely too high. It is not applicable to alum powders even with the correction made above. For a rough method it answers fairly well and it is quite easy of execution.

## ESTIMATION OF PHOSPHORIC ACID.

This determination was made in the same manner as in fertilizers, as prescribed by the Association of Official Agricultural Chemists at their last meeting, as follows :‡

Weigh out 2 grams. of the sample, ignite carefully in a muffle, and treat with 30 cubic centimeters concentrated nitric acid.

Boil gently until all phosphates are dissolved and all organic matter destroyed ; dilute to 200 cubic centimeters ; mix and pass through a dry filter ; take 50 cubic centimeters of filtrate ; neutralize with ammonia. To the hot solutions for every decigram. of  $\text{P}_2\text{O}_5$  that is present add 50 cubic centimeters of molybdic solution. Digest at about 65° C. for one hour, filter, and wash with water or ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution.) Dissolve the

\* Fully described in Bull. No. 15, p. 32.

† Communicated to the author in MSS.

‡ Bull. No. 19, Chem. Div. U. S. Dep't Ag'l, p. 58.

precipitate on the filter with ammonia and hot water and wash into a beaker to a bulk of not more than 100 cubic centimeters. Nearly neutralize with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 cubic centimeters of ammonia solution of density 0.95. Let stand several hours (two hours are usually enough.) Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

#### ESTIMATION OF TARTARIC ACID.

The method used in this estimation was that known as the "Goldenberg Geromont," which is described in full in *Chemiker Zeitung* 12, 1888, 390. This and other methods for the estimation of tartaric acid in crude argol and other raw materials were lately submitted to a critical comparison in the tartrate factory at Nienburg; the Goldenberg Geromont method avoided the principal sources of error and is recommended as the best and most easy of execution.

The procedure as modified for application to a tartate baking-powder is as follows:—

Weigh out 5 grams., wash into a 500-cubic centimeter flask with about 100 cubic centimeters of water; add 15 cubic centimeters of strong hydrochloric acid; make up to mark and allow the starch to settle. Filter, measure out 50 cubic centimeters of the clear filtrate; add to it 10 cubic centimeters of a solution of carbonate of potash containing 300 grams.  $K_2CO_3$  to the liter and boil half an hour; filter into a porcelain dish and evaporate filtrate and washings to a bulk of about 10 cubic centimeters. Add gradually with constant stirring 4 cubic centimeters glacial acetic acid, and then 100 cubic centimeters of 95 per cent. alcohol, stirring the liquid until the precipitate floating in it assumes a crystalline appearance. After it has stood long enough for this precipitate to form and settle, best for several hours, decant through a small filter, add alcohol to the precipitate, bring it on the filter, wash out the dish and finally the filter carefully, with alcohol, until it is entirely free from acetic acid. Transfer filter and precipitate to a beaker, add water and boil, washing out the dish also with boiling water if any of the precipitate adheres to it. The resulting solution is titrated with decinormal alkali solution using phenol-phthalein as indicator; 1 cubic centimeter decinormal alkali correspond to .0188 grams. of potassium bitartrate, or .0150 grams. of tartaric acid.

#### ESTIMATION OF ALKALIES.

The estimation of the soda and potash in the powders was carried out by separating them as chlorides, determining the potash as potassium platonic chloride and calculating the difference as sodium chloride. The detailed procedure was similar to that used by the Association of Official Agricultural Chemists for determining potash in fertilizers, as follows:

Weigh out 5 grams. into a platinum dish and incinerate in a muffle at a low heat. The charred mass is well rubbed up in a mortar, then boiled 15 minutes with about 200 cubic centimeters of water to which has been added a little hydrochloric acid. The whole is transferred to a 500-cubic centimeter flask and after cooling made up to the mark and filtered. Of the filtered liquid 100 cubic centimeters, representing 1 gram. of the sample, are measured out, heated in the water bath, and slight excess of barium

\* *Chemiker Zeitung* 13, 1889, 160.

chloride added; then without filtering barium hydrate is added in slight excess, the precipitate filtered off and washed. To the filtrate is added a little ammonium hydrate and then ammonium carbonate until all the barium is precipitated. This precipitate is filtered and washed, the filtrate evaporated to dryness and carefully ignited until all volatile matter is driven off, when it is weighed. This gives the weight of the mixed chlorides. The residue is taken up with hot water, from 5 to 10 cubic centimeters of a 10 per cent. solution of platinic chloride added, and the whole evaporated to a syrupy consistence in the water bath; then it is treated with strong alcohol, the precipitate washed with alcohol by decantation, transferred to a Gooch crucible, dried at  $100^{\circ}\text{C}.$ , and weighed. The weight of the precipitate multiplied by  $\cdot 19308$  gives the weight of  $\text{K}_2\text{O}$ , and by  $\cdot 3056$  the equivalent amount of  $\text{KCl}$ . The weight of  $\text{KCl}$  found is subtracted from the weight of the mixed chloride, the remainder being the  $\text{NaCl}$ , which multiplied by  $\cdot 5300$  gives the weight of  $\text{Na}_2\text{O}$  in the sample.

#### ESTIMATION OF ALUMINIUM.

In the case of a "straight" alum powder, the simple estimation by burning to ash, extracting, and determining the alum by direct precipitation with ammonia would probably be accurate, but in view of the frequent use of flour as a "filler," as well as of the presence of calcium as an impurity, it is best, even with those made up with alum alone, to use a method which will insure a complete separation of the alum. The following procedure, given by Allen for the quantitative estimation of alum in bread, was found to give good results with baking-powders:

Take 5 grams. and incinerate in a muffle, The heat should be moderate so as not to fuse the ash. The process is completed by adding pure sodium carbonate and a little nitre, and heating the mixture to fusion. The product is rinsed out with water into a beaker, acidulated with hydrochloric acid, and evaporated to dryness. The residue is taken up with dilute acid, the liquid made up to 500 cubic centimeters in a graduated flask, filtered, and 50 cubic centimeters taken for precipitation. To the solution dilute ammonia is added until the precipitate barely redissolves on stirring, when a slightly acid solution of ammonium acetate is added, and the liquid brought to a boil. After a few minutes' heating the solution should be set aside for some hours, when its appearance should be observed. (If gelatinous it probably consists solely of iron and alum phosphates, but if granular more or less of the earthy phosphates have been co-precipitated; then it should be separated, redissolved in dilute hydrochloric acid, the solution again neutralized with ammonia, and treated with ammonium acetate.) The precipitate of iron and aluminium phosphates is filtered off, washed, and redissolved in the smallest quantity of hydrochloric acid. The resultant solution is poured into an excess of an aqueous solution of *pure* caustic soda contained in a platinum or nickel vessel. After heating for some time, the liquid is considerably diluted and filtered. The filtrate is acidulated with hydrochloric acid, ammonium acetate and a few drops of sodium phosphate added, and then a slight excess of ammonia. The liquid is kept hot till all smell of ammonia is lost, when it is filtered, and the precipitated aluminium phosphate washed, ignited, and weighed. Its weight multiplied by  $3.713$  gives the ammonia alum (hydrated), or by  $3.873$  the potash alum in the 5 grams. of sample taken.

In the phosphate and alum powders the above method gave a fairly good separation of the alum, but the following separation by means of molybdenum was found to be more exact, and at the same time much more convenient of application.

Weigh out 5 grams. into a platinum dish, char, treat with strong nitric acid, and filter into a 500 cubic centimeter flask. After washing the residue slightly, transfer filter and all back to the platinum dish and burn to whiteness. To the ash add mixed carbonates and fuse. Take up with nitric acid, evaporate to dryness, acidify again with nitric acid, and wash all into the 500 cubic centimeter flask. Nearly neutralize the contents of the flask with ammonia, and add molybdate of ammonium sufficient to precipitate all the phosphoric acid present. Allow to stand some time, make up to the mark, shake thoroughly, and filter off 100 cubic centimeters through a dry filter. This is exactly neutralized with ammonia, keeping the solution as cool as possible to avoid the deposition of molybdic acid. Filter and wash the precipitate, redissolve in dilute nitric acid with the addition of a little ammonium nitrate, and precipitate as before. Filter through a paper filter, burn, ignite, and weigh as  $Al_2O_3$ . The alumina and phosphoric acid may be determined in the same sample by the above method, modifying it as follows: When the solution, ash, etc., have all been brought into the graduated flask, make up to the mark without adding molybdate, filter and take 100 cubic centimeters, nearly neutralize with ammonia, add ammonium nitrate and molybdate of ammonium, digest and filter. The filtrate contains the aluminium and may be precipitated with ammonia as above, while the phosphoric acid is all contained in the precipitate, which may be redissolved in ammonia and precipitated with magnesia mixture.

#### ESTIMATION OF CALCIUM.

This determination was made as follows:—Weigh out 5 grams. of the sample, transfer to a 500 cubic centimeter flask, add 40 or 50 cubic centimeters of water, and then 20 or 30 cubic centimeters of strong hydrochloric acid. Make up to the mark with water, shake thoroughly, and set aside to allow starch to settle. Filter through a dry filter, and take aliquot parts of the filtrate for precipitation; in phosphate powders not more than 50 cubic centimeters should be used. Nearly neutralize with ammonia, acidify slightly with acetic acid, add ammonia acetate, and boil. Filter from the precipitate, if there be any, add ammonium oxalate, and allow to stand several hours. Filter into a Gooch crucible, and dry at  $100^{\circ}$ . Weigh as oxalate.

#### ESTIMATION OF SULPHURIC ACID.

The sulphuric acid was estimated without previous ignition of the powder, as follows:—

Weigh out .5 to 1 gram. of the powder, according to its character, the former quantity being more convenient for alum powders, and transfer to a beaker. Digest with strong hydrochloric acid until all of the powder, including the starch, goes into solution; add barium chloride to slight excess while still hot, and allow it to stand for twelve hours, or over night. Filter into a Gooch crucible, ignite, and weigh.

#### ESTIMATION OF AMMONIA.

Ammonia is present either as bicarbonate, or as ammonium sulphate in the alum

powders. The estimation was made by the Kjeldahl method, as used by the Association of Official Agricultural Chemists.\* Where flour instead of starch is used as a filling the gluten would give ammonia, of course, and wherever a tartrate powder was found to give any appreciable amount of ammonia by the method, a weighed portion was taken, water added, the solution filtered from the starch, and subjected to analysis. The results were practically the same as those obtained directly from the powder. Probably flour is not often used. In the case of the alum powders, the difference that would be made by flour filling was disregarded, as the amount of alum present is sufficiently established by the percentage of aluminium oxide and sulphuric acid found; the amount of ammonia found was almost invariably low in proportion to these other constituents of ammonia alum.

#### ESTIMATION OF MOISTURE.

The percentage of water of association and combination as given in the analyses was obtained by difference. A number of attempts were made to estimate it directly in the following way: A weighed portion of the sample was placed in a U tube, which was kept immersed in boiling water. At one end this tube was connected with a series of sulphuric acid wash-bottles, and at the other with weighed potash bulbs filled with sulphuric acid, and beyond these with an aspirator. In this way a current of dried air was drawn through the sample while it was kept at 100° C., and the water drawn from it in this way was absorbed by the sulphuric acid in the potash bulb, while the carbonic acid was drawn into the aspirator. The increase in weight of the potash bulbs gave the weight of water absorbed. It was found, however, that the sample would cake into a hard mass, through which a channel would form which would permit the passage of the current of dry air, without affecting the greater mass of the powder, and no exact results could be obtained. Some improvement was made by mixing the powder with dry oxide of zinc, so as to prevent the formation of a channel, but still the results were not at all satisfactory, and the attempt to make a direct estimation was finally abandoned. Even if the determination could be made exact, it is doubtful if all the water of combination could be obtained at 100° C., especially in phosphate and alum powders, and probably a temperature high enough to accomplish this would effect a decomposition of the starch.

#### EXPRESSION OF THE RESULTS OF ANALYSIS.

The results of analysis are given, first, as acid and basic radicals in percentage composition, while in the second part of each table an attempt has been made to combine these into salts showing the constitution of the powder. The difficulties attending this calculation of the probable combination of the acids and bases were so great that I was frequently tempted to give it up entirely and state only percentage composition. I finally concluded to insert the calculation with the proviso that it should be considered at best merely an approximation to the exact composition of the powder. The obstacles in the way of an exact calculation may be stated as follows: In the first place the amount of total carbonic acid found is always less than that required to form bicarbonate of soda with the amount of sodium oxide found. This is undoubtedly due to a partial action of the acid constituent of the powder upon the bicarbonate, by which carbonic acid has been

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\* Fully described in Bull. No. 19. Chem. Div. U. S. Dep't Agriculture.

lost. The percentage of bicarbonate is therefore calculated from the per cent. of carbonic acid found, and the excess of sodium oxide left is stated as "residual" sodium oxide, without attempting to make further hypotheses as to the results of its combination with the acid constituent. It is possible that part of the bicarbonate may become converted into the normal carbonate under the conditions of being mixed and in contact with other chemicals, though this is not likely; then the indefinite composition of many of the commercial salts used in the powders renders it an extremely difficult matter to arrive at any satisfactory conclusion as to the make up of the powder in which they are used. The acid phosphate of lime, for instance, is a very variable substance, and even ammonia alum, which might reasonably be supposed to be constant in its composition, is found to vary widely from the theoretical. Its content of water varies according to the greater or less amount of drying it has undergone, and aside from this the ratios of the ammonia, sulphuric acid, and alumina to one another are at variance with the formula.

This is shown by the following analysis of a sample of commercial ammonia alum obtained in a powdered condition:

*Analysis of commercial ammonia alum.*

| Constituents.                                    | Found.           | Theoretical Composition. |
|--|------------------|--------------------------|
|  | <i>Per cent.</i> | <i>Per cent.</i>         |
| Aluminium oxide, $\text{Al}_2\text{O}_3$ .. .. . | 12.62            | 11.36                    |
| Sulphuric Acid, $\text{SO}_3$ .. .. .            | 34.17            | 35.28                    |
| Ammonia, $\text{NH}_3$ .. .. .                   | 2.75             | 3.75                     |
| Water of crystallization (by difference) .. .. . | 50.46            | 49.61                    |
|  | 100.00           | 100.00                   |

This indicates that the commercial salt is somewhat basic as regards the alumina, yet there is a deficiency of ammonia, so that if the former is all combined with sulphuric acid as normal sulphate, there is still not sufficient of the acid left for combination with the ammonia, although the latter is present in too low a proportion to the other constituents. This anomaly holds good throughout many of the samples.

I have expressed the sum total of the alumina, sulphuric acid, and ammonia as "anhydrous ammonia alum," combining the sulphuric acid, first with the alumina as far as it went, and the rest with the ammonia, and where there was not sufficient for combination with all the ammonia adding the latter as ammonia.

The presence of acid phosphate of lime still further complicates this calculation, as it is a question how much of the sulphuric acid should be taken from the alum to combine with part of the lime as sulphate of lime.

In the expression of the results where acid phosphate of lime is present, I have combined the lime with phosphoric acid as normal phosphate as far as it went, and added the rest as free phosphoric acid, grouping the whole together and calling it "acid phosphate of lime." Following is an analysis of a sample of commercial acid phosphate of lime, obtained from the trade:

*Analysis of commercial acid phosphate of lime.*

|   | <i>Per cent.</i> |
|---|------------------|
| Calcium Oxide, $\text{CaO}$ .. .. .             | 24.93            |
| Phosphoric acid, $\text{P}_2\text{O}_5$ .. .. . | 52.45            |
| Sulphuric acid, $\text{SO}_3$ .. .. .           | .15              |
| Water .. .. .                                   | 22.80            |
|   | 100.33           |

In this sample the ratio of lime to phosphoric acid is about 1 : 2, and this relation holds good in many of the powders containing the phosphate, but in some it is quite different. The above sample is almost free from sulphate of lime, while many of the powders show considerable quantities of it, indicating that all the acid phosphates are not so pure in this respect. Chemists will readily understand the impossibility of giving the proportions of the various forms of lime phosphates contained in such a substance. As given in the tables the relative acidity is shown, though of course the phosphoric acid does not occur as free acid.

Both the alum and the lime phosphate contain large percentages of water, hygroscopic moisture in the latter, and crystallisation water in the former, so that the per cents. of the "anhydrous" salts given are always lower than the proportions of the hydrated salts originally used in compounding the powder. Nearly half the weight of the alum is crystallisation water, some part of which is probably driven off in some cases when it is used for baking-powder purposes, but there are no means of ascertaining how much, and of course the moisture in the acid phosphate would vary in different samples, so there is no possible way of approximating the amounts of the hydrated substances, as they were originally used.

Ammonia bicarbonate is another substance of indefinite composition. As given in the tables, it has been calculated from the ammonia found, upon the assumed composition given it in the U.S. Pharmacopœia, viz.,  $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_3 \cdot \text{NH}_2\text{CO}_2$ .

In case ammonia carbonate were present in any of the powders containing ammonia alum, I know of no way of estimating the amount or even the fact of its presence in the small quantities used.

The percentage of "available carbonic acid" is placed first in the tables as constituting the most important indication of the efficiency of the sample as an aerating agent.

## ON THE DENSITIES AND REFRACTIVE INDICES OF CERTAIN OILS.

By J. H. LONG.

(Concluded.)

| <i>Olive Oil, 1.</i> |       |        |                 | <i>Olive Oil, 11.</i> |       |        |                 |
|----------------------|-------|--------|-----------------|-----------------------|-------|--------|-----------------|
| T.                   | D.    | N.     | $\frac{N-1}{D}$ | T.                    | D.    | N.     | $\frac{N-1}{D}$ |
| 18                   | ·9141 | 1·4702 | ·5144           | 18                    | ·9139 | 1·4719 | ·5164           |
| 19                   | ·9134 | 1·4698 | ·5143           | 19                    | ·9133 | 1·4715 | ·5163           |
| 20                   | ·9127 | 1·4695 | ·5143           | 20                    | ·9126 | 1·4711 | ·5162           |
| 21                   | ·9121 | 1·4691 | ·5143           | 21                    | ·9119 | 1·4707 | ·5162           |
| 22                   | ·9114 | 1·4688 | ·5144           | 22                    | ·9112 | 1·4703 | ·5161           |
| 23                   | ·9107 | 1·4684 | ·5143           | 23                    | ·9106 | 1·4698 | ·5159           |
| 24                   | ·9101 | 1·4680 | ·5142           | 24                    | ·9099 | 1·4694 | ·5159           |
| 25                   | ·9094 | 1·4677 | ·5143           | 25                    | ·9093 | 1·4690 | ·5158           |
| 30                   | ·9061 | 1·4658 | ·5142           | 30                    | ·9060 | 1·4669 | ·5153           |
| 35                   | ·9028 | 1·4640 | ·5140           | 35                    | ·9027 | 1·4648 | ·5148           |

*Olive Oil, 10.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9142 | 1.4718 | .5161           |
| 19 | 9135 | 1.4714 | .5160           |
| 20 | 9129 | 1.4709 | .5158           |
| 21 | 9122 | 1.4705 | .5158           |
| 22 | 9115 | 1.4701 | .5157           |
| 23 | 9109 | 1.4696 | .5155           |
| 24 | 9102 | 1.4692 | .5155           |
| 25 | 9095 | 1.4688 | .5154           |
| 30 | 9062 | 1.4666 | .5149           |
| 35 | 9029 | 1.4645 | .5148           |

*Olive Oil, 5.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9149 | 1.4704 | .5142           |
| 19 | 9142 | 1.4701 | .5142           |
| 20 | 9136 | 1.4697 | .5141           |
| 21 | 9129 | 1.4693 | .5141           |
| 22 | 9122 | 1.4690 | .5141           |
| 23 | 9116 | 1.4685 | .5140           |
| 24 | 9109 | 1.4682 | .5140           |
| 25 | 9103 | 1.4678 | .5139           |
| 30 | 9069 | 1.4659 | .5137           |
| 35 | 9036 | 1.4640 | .5135           |

*Cotton-seed Oil, 6.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9199 | 1.4735 | .5147           |
| 19 | 9192 | 1.4731 | .5147           |
| 20 | 9186 | 1.4727 | .5146           |
| 21 | 9179 | 1.4724 | .5147           |
| 22 | 9172 | 1.4720 | .5147           |
| 23 | 9165 | 1.4716 | .5146           |
| 24 | 9158 | 1.4712 | .5145           |
| 25 | 9151 | 1.4709 | .5147           |
| 30 | 9118 | 1.4690 | .5144           |
| 35 | 9084 | 1.4671 | .5142           |

*Cotton-seed Oil, 8.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9199 | 1.4749 | .5163           |
| 19 | 9193 | 1.4745 | .5162           |
| 20 | 9186 | 1.4741 | .5161           |
| 21 | 9179 | 1.4737 | .5161           |
| 22 | 9172 | 1.4733 | .5160           |
| 23 | 9165 | 1.4729 | .5160           |
| 24 | 9159 | 1.4725 | .5159           |
| 25 | 9151 | 1.4721 | .5159           |
| 30 | 9118 | 1.4700 | .5155           |
| 35 | 9084 | 1.4680 | .5152           |

*Cotton-seed Oil, 7.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9224 | 1.4729 | .5127           |
| 19 | 9217 | 1.4725 | .5127           |
| 20 | 9210 | 1.4722 | .5127           |
| 21 | 9203 | 1.4718 | .5127           |
| 22 | 9196 | 1.4715 | .5127           |
| 23 | 9190 | 1.4711 | .5126           |
| 24 | 9183 | 1.4708 | .5127           |
| 25 | 9176 | 1.4704 | .5127           |
| 30 | 9142 | 1.4687 | .5127           |
| 35 | 9109 | 1.4670 | .5127           |

*Cotton-seed Oil, 9.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9201 | 1.4737 | .5148           |
| 19 | 9194 | 1.4733 | .5148           |
| 20 | 9188 | 1.4730 | .5148           |
| 21 | 9180 | 1.4726 | .5148           |
| 22 | 9174 | 1.4722 | .5147           |
| 23 | 9167 | 1.4718 | .5147           |
| 24 | 9160 | 1.4714 | .5146           |
| 25 | 9154 | 1.4710 | .5145           |
| 30 | 9119 | 1.4690 | .5143           |
| 35 | 9085 | 1.4671 | .5141           |

*Cotton-seed Oil, 12.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9203 |        |                 |
| 19 | 9196 |        |                 |
| 20 | 9190 |        |                 |
| 21 | 9183 | 1.4708 | .5127           |
| 22 | 9176 |        |                 |
| 23 | 9170 | 1.4700 | .5125           |
| 24 | 9163 |        |                 |
| 25 | 9157 |        |                 |
| 30 | 9124 |        |                 |
| 35 | 9090 |        |                 |

*Sesamé Oil, 4.*

| T. | D.   | N.     | $\frac{N-1}{D}$ |
|----|------|--------|-----------------|
| 18 | 9208 | 1.4742 | .5150           |
| 19 | 9201 | 1.4738 | .5149           |
| 20 | 9194 | 1.4735 | .5150           |
| 21 | 9188 | 1.4731 | .5149           |
| 22 | 9181 | 1.4727 | .5149           |
| 23 | 9174 | 1.4723 | .5148           |
| 24 | 9167 | 1.4719 | .5148           |
| 25 | 9161 | 1.4715 | .5147           |
| 30 | 9127 | 1.4696 | .5145           |
| 35 | 9093 | 1.4677 | .5144           |



*Cotton-seed Oil, 16.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9203 | 1·4747 | ·5158           |
| 19 | ·9196 | 1·4743 | ·5158           |
| 20 | ·9189 | 1·4739 | ·5157           |
| 21 | ·9182 | 1·4735 | ·5157           |
| 22 | ·9176 | 1·4731 | ·5156           |
| 23 | ·9168 | 1·4727 | ·5156           |
| 24 | ·9162 | 1·4723 | ·5155           |
| 25 | ·9155 | 1·4719 | ·5155           |
| 30 | ·9120 | 1·4699 | ·5153           |
| 35 | ·9086 | 1·4679 | ·5150           |

*Sesamé Oil, 18.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9195 | 1·4744 | ·5159           |
| 19 | ·9188 | 1·4740 | ·5159           |
| 20 | ·9181 | 1·4736 | ·5158           |
| 21 | ·9174 | 1·4732 | ·5158           |
| 22 | ·9167 | 1·4728 | ·5158           |
| 23 | ·9160 | 1·4724 | ·5157           |
| 24 | ·9154 | 1·4720 | ·5157           |
| 25 | ·9147 | 1·4716 | ·5156           |
| 30 | ·9113 | 1·4695 | ·5152           |
| 35 | ·9078 | 1·4675 | ·5150           |

*Mustard Oil, 2.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9129 | 1·4749 | ·5203           |
| 19 | ·9123 | 1·4745 | ·5201           |
| 20 | ·9116 | 1·4741 | ·5201           |
| 21 | ·9109 | 1·4737 | ·5199           |
| 22 | ·9103 | 1·4733 | ·5199           |
| 23 | ·9097 | 1·4729 | ·5198           |
| 24 | ·9090 | 1·4725 | ·5198           |
| 25 | ·9084 | 1·4722 | ·5198           |
| 30 | ·9052 | 1·4702 | ·5194           |
| 35 | ·9020 | 1·4683 | ·5192           |

*Castor Oil, 3.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9602 | 1·4799 | ·4998           |
| 19 | ·9595 | 1·4795 | ·4997           |
| 20 | ·9589 | 1·4791 | ·4996           |
| 21 | ·9582 | 1·4788 | ·4997           |
| 22 | ·9575 | 1·4784 | ·4996           |
| 23 | ·9569 | 1·4780 | ·4995           |
| 24 | ·9562 | 1·4777 | ·4996           |
| 25 | ·9555 | 1·4773 | ·4995           |
| 30 | ·9522 | 1·4755 | ·4994           |
| 35 | ·9488 | 1·4738 | ·4994           |

*Sesamé Oil, 14.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9212 | 1·4756 | ·5163           |
| 19 | ·9206 | 1·4752 | ·5162           |
| 20 | ·9199 | 1·4748 | ·5161           |
| 21 | ·9192 | 1·4744 | ·5161           |
| 22 | ·9185 | 1·4740 | ·5161           |
| 23 | ·9179 | 1·4736 | ·5160           |
| 24 | ·9172 | 1·4732 | ·5159           |
| 25 | ·9165 | 1·4728 | ·5159           |
| 30 | ·9132 | 1·4708 | ·5156           |
| 35 | ·9098 | 1·4688 | ·5153           |

*Mustard Oil, 15.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9140 | 1·4754 | ·5201           |
| 19 | ·9133 | 1·4750 | ·5201           |
| 20 | ·9127 | 1·4746 | ·5200           |
| 21 | ·9120 | 1·4742 | ·5200           |
| 22 | ·9113 | 1·4738 | ·5199           |
| 23 | ·9107 | 1·4733 | ·5197           |
| 24 | ·9100 | 1·4730 | ·5198           |
| 25 | ·9094 | 1·4726 | ·5197           |
| 30 | ·9060 | 1·4705 | ·5193           |
| 35 | ·9028 | 1·4685 | ·5189           |

*Mustard Oil, 17.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9132 | 1·4748 | ·5199           |
| 19 | ·9125 | 1·4744 | ·5199           |
| 20 | ·9119 | 1·4740 | ·5198           |
| 21 | ·9112 | 1·4736 | ·5198           |
| 22 | ·9106 | 1·4732 | ·5197           |
| 23 | ·9099 | 1·4728 | ·5196           |
| 24 | ·9093 | 1·4724 | ·5195           |
| 25 | ·9086 | 1·4721 | ·5196           |
| 30 | ·9053 | 1·4701 | ·5193           |
| 35 | ·9021 | 1·4681 | ·5189           |

*Lard Oil, 13.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9137 | 1·4694 | ·5137           |
| 19 | ·9130 | 1·4690 | ·5137           |
| 20 | ·9122 | 1·4686 | ·5137           |
| 21 | ·9116 | 1·4682 | ·5136           |
| 22 | ·9109 | 1·4678 | ·5136           |
| 23 | ·9102 | 1·4674 | ·5135           |
| 24 | ·9095 | 1·4670 | ·5135           |
| 25 | ·9088 | 1·4666 | ·5134           |
| 30 | ·9053 | 1·4647 | ·5133           |
| 35 | ·9019 | 1·4627 | ·5130           |

*Peanut Oil, 19.*

| T. | D.    | N.     | $\frac{N-1}{D}$ |
|----|-------|--------|-----------------|
| 18 | ·9187 | 1·4725 | ·5143           |
| 19 | ·9180 | 1·4721 | ·5143           |
| 20 | ·9173 | 1·4717 | ·5142           |
| 21 | ·9164 | 1·4713 | ·5143           |
| 22 | ·9157 | 1·4709 | ·5143           |
| 23 | ·9151 | 1·4705 | ·5142           |
| 24 | ·9144 | 1·4701 | ·5141           |
| 25 | ·9138 | 1·4696 | ·5139           |
| 30 | ·9103 | 1·4678 | ·5139           |
| 35 | ·9069 | 1·4658 | ·5136           |

The numbers in the column headed  $\frac{N-1}{D}$  are not quite constant, but do not vary more than is the case with many organic substances. In most cases the refractive index seems to decrease somewhat more rapidly than does the specific gravity.

The saponification equivalents found for several of these oils, sesamé, olive, and cotton-seed, show a mean molecular weight of about 870. From this the *molecular* refractive energy,  $M \left( \frac{N-1}{D} \right)$ , is about 448, which coincides very well with the atomic refractive energies, C=4·85, H=1·50, and O=3.

If an oil in the above table contained only tri-olein these numbers would lead to 450·4. A mixture of tri-olein and tri-stearin would yield nearly the same result; while tri-palmitin, having a lower molecular weight, would make the number slightly smaller. A mixture of 8 parts of tri-olein and 2 parts of tripalmitin would give 447·2, and this is approximately the composition of the above oils.

In the olive oils the specific gravity at 20° C. varies between ·9126 and ·9136. These values are about the same as commonly given for the finest cold-pressed oils, and are within the limits of the United States and British Pharmacopœias. Schaedler gives ·9143 as the specific gravity of a pure sample at 20°, but states that in hot-pressed oils rich in palmitin it may be as high as ·922 at the same temperature. The refractive indices at 20° vary from 1·4695 to 1·4711, and the specific refractive energy from ·5143 to ·5162 at the same temperature.

In the six samples of cotton-seed oil examined the variations in the specific gravity at 20° are between ·9186 and ·9210. These numbers are all greater than those with olive oil. The refractive indices vary from 1·4722 to 1·4741, and the refractive energies between ·5127 and ·5161 at 20°. These last numbers are nearly the same as with olive oil.

It will be noticed that the values given for the specific gravity are much lower than those usually quoted. Allen places the density of the crude oil between ·928 and ·930, with that of the refined between ·922 and ·926. Dietrich (*Dingler's Poly. Jour.*, 1885, 127) places the density of the pure oil at 23° between ·917 and ·921. These numbers have evidently been obtained from samples richer in palmitin than were those examined by me.

In the three samples of sesamé oil the specific gravity at 20° varies between ·9181

and .9199, the refractive indices between 1.4735 and 1.4748, and the quotient  $\frac{N-1}{D}$  between .5150 and .5161. These numbers are similar to those for cotton-seed oil.

In mustard oil the density is lower; at 20° the three samples vary between .9116 and .9127, their refractive indices between 1.4740 and 1.4746, and the refractive energies between .5198 and .5201. These figures are higher than found for other oils, and may have a practical value. In castor oil we have a high gravity and low refractive energy.

The specific gravities found for lard oil and peanut oil do not differ materially from those usually given, and there seems to be nothing unusual about the refraction.

In many cases determinations of refractive index have a practical use in the identification of organic liquids, and also in quantitative valuation.

Alex. Müller has recently proposed the use of the Abbé refractometer in the examination of butter, and Skulweit (*Rept. Anal. Chem.* 1886, pp. 181 and 235) has carried out a number of tests to show the value of the method. It appears from his tests that *butter oleine* (separated after melting by partial cooling and pressure) has a lower refractive index than any oil in the above table, and also lower than that of the various solid products, as butterine and oleomargarine.

Skulweit's observations have undoubtedly a practical value, but his method necessitates the use of the Abbé refractometer. I have found that results almost as sharp can be obtained by using solutions of the fats made with definite mixtures of alcohol and chloroform, and determining the minimum deviation in the usual manner with the Meyerstein or similar instrument. The above experiments show that a determination of the refractive power, coupled with that of the specific gravity, may prove of value in the identification of other fatty oils.

## ON THE BEHAVIOUR OF PHENOL-PHTHALEIN WITH AMMONIA.

By J. H. LONG.\*

THE peculiar action of ammonia on phenol-phthalein was first pointed out by Beckurts, I believe, in a paper in the *Pharmaceutische Centralhalle*. Soon after the experiments of Luck† were published, showing the great value of this substance as an indicator, it came into general use in Germany, and was even incorporated among the tests of a new edition of the German Pharmacopœia then published. Schlickum, in his "Commentary on the German Pharmacopœia," 2nd ed., states in one place that the behaviour of litmus and phenol-phthalein in the titration of acids with ammonia water is the same, while in another place he remarks that the presence of ammonium salts interferes somewhat with the delicacy of the titration when phenol-phthalein is the indicator. Beckurts shows the error into which a number of writers had fallen in this regard, by giving a series of tests carried out with different indicators. In the following year, Flückiger‡ published experiments on the sensitiveness of phenol-phthalein, leading to the conclusion that it could not be employed with ammoniacal solutions. In the excellent papers by Thomson,§ a similar conclusion is reached.

In the *Pharmacist* I published the results of a long series of experiments on the action of phenol-phthalein, and among other points, I touched on the want of delicacy with ammonia. In that paper I offered an explanation of this behaviour, suggested in part by a remark of Baeyer\* on the formation of phenol-di-imido-phthalein,

\* *American Chemical Journal*.

† *Ztschr. anal. Chem.* 1877, 332.

‡ *Ber. d. chem. Gessell.* 17, 592. Ref.

§ *Chem. News*, 47, 125, 135 and 181.

\* *Ber. d. chem. Gessell.* 11, 1297.

and partially confirmed this explanation by a number of experiments. Since then I have again taken up the subject, repeating the old experiments and adding new ones, which I think afford a full confirmation of my former suggestion. It is this later work which I wish to present here in detail.

When a few drops of an alcoholic solution of phenol-phthalein are added to a strong solution of soda, the deep red colour which forms at first, vanishes in a short time—within a minute, if the soda is sufficiently strong. The colour can be restored by partial neutralisation with acids. When the indicator is added to strong ammonia solution (26 per cent.), a red colour is produced which is more permanent, fading completely only after hours or days.

In this case, that is, after the *complete* disappearance of the colour, addition of acid produces no change. If the acid is added before the colour is fully discharged it becomes much brighter.

When phenol-phthalein is added to a very weak soda solution, the red colour produced seems to be indefinitely permanent; but with weak ammonia it vanishes sooner or later, the interval between the mixing of the solutions and the disappearance of colour depending on several factors, as dilution, temperature, and strength of indicator.

There are, therefore, important differences between the action of soda and that of ammonia on phenol-phthalein. If to a definite amount of a standard solution of hydrochloric acid containing a few drops of the indicator, standard ammonia solution be added, something more than the theoretical amount of the latter must be used to give the permanent red colour. However, by increasing the amount of indicator added, or by cooling the solutions, the colour can be obtained by nearly or quite the equivalent number of c.c. of ammonia.

A similar result is obtained by adding soda solution to a solution containing, along with free mineral acid, some salt of ammonium and the indicator. The effect of temperature was shown by the following experiments. I prepared half normal solutions of hydrochloric acid and sodium hydroxide and a solution of ammonium chloride containing 100 grms. in one litre. I took now 25 c.c. of the acid, 10 c.c. of the ammonium chloride, 65 c.c. of water, and a few drops of the indicator. To the mixture, slightly less than 25 c.c. of the sodium hydroxide was added, the whole was cooled to the desired temperature, and then more sodium hydroxide was run in to colouration. The results obtained at various temperatures are given in this table:—

| Temperature. | c.c. $\frac{N}{2}$ NaOH. | Temperature. | c.c. $\frac{N}{2}$ NaOH. |
|--------------|--------------------------|--------------|--------------------------|
| 6.5          | 26.2                     | 49.5         | 29.9                     |
| 13.5         | 27.0                     | 62.0         | 31.0                     |
| 22.5         | 27.6                     | 69.1         | 32.0                     |
| 30.0         | 28.1                     | 76.0         | 32.8                     |
| 38.0         | 28.7                     |              |                          |

The final reaction was in no case as sharp as in a titration between the alkali and acid alone, but the results are close approximations. Something similar is shown in the following experiments, which disclose likewise the effects of excess of ammonium chloride. Here I employed normal solutions of hydrochloric acid, sodium hydroxide, and ammonium chloride, and for each experiment took 25 c.c. of acid, a definite quantity of ammonium chloride, and added enough water to make 100 c.c. In each case 1 c.c. of a one-tenth per cent. solution of phenol-phthalein was added, and then caustic soda from a burette to colouration.

The solution in the beaker was kept at a temperature of 0° C., and that in the burette as near this as possible. The experiments were repeated for each mixture three times, and gave closely agreeing results, the end reactions being quite satisfactory and sharp. In the following table the mean of the results from the three tests is given:—

| No. | HCl.<br>c.c. | NH <sub>4</sub> Cl.<br>c.c. | H <sub>2</sub> O.<br>c.c. | NaOH req'd.<br>c.c. |
|-----|--------------|-----------------------------|---------------------------|---------------------|
| 1   | 25           | 5                           | 70                        | 25                  |
| 2   | 25           | 10                          | 65                        | 25.08               |
| 3   | 25           | 15                          | 60                        | 25.20               |
| 4   | 25           | 25                          | 50                        | 25.28               |
| 5   | 25           | 30                          | 45                        | 25.37               |
| 6   | 25           | 50                          | 25                        | 25.68               |

These experiments show clearly that with the temperature sufficiently low, the disturbing action of small amounts of ammonium salts is very slight. They show also at what rate the disturbance increases with increasing amounts of ammonium chloride.

At a temperature of 20° C. I obtained the following results, working with the same solutions:—

| No. | HCl.<br>c.c. | NH <sub>4</sub> Cl.<br>c.c. | H <sub>2</sub> O.<br>c.c. | NaOH req'd.<br>c.c. |
|-----|--------------|-----------------------------|---------------------------|---------------------|
| 1   | 25           | 5                           | 70                        | 25.22               |
| 2   | 25           | 10                          | 65                        | 25.38               |
| 3   | 25           | 15                          | 60                        | 25.61               |
| 4   | 25           | 20                          | 55                        | 25.82               |
| 5   | 25           | 25                          | 50                        | 25.98               |

We find here differences in the amount of alkali required, varying between .2 c.c. for the weakest solution to 1 c.c. for that containing 25 c.c. of ammonium chloride, which amounts to an error of 4 per cent. In all these cases the error is so large that it could not be neglected in any kind of practical work. However, by employing a larger amount of indicator, the error can be almost entirely corrected, as shown by the following tests:—

I used here 25 c.c. of the acid and 5 c.c. of the ammonium chloride solution at a temperature of 20° C.

1. With 2 c.c. of indicator required 25.12 c.c. NaOH.
2. With 4 c.c. of indicator required 25.02 c.c. NaOH.
3. With 6 c.c. of indicator required 25.00 c.c. NaOH.

By using larger amounts of the indicator, the final reaction is obtained with satisfactory sharpness.

*(To be continued.)*

## REVIEWS.

WATT'S MANUAL OF CHEMISTRY THEORETICAL AND PRACTICAL (BASED ON FOWNES' MANUAL).

VOL. I. PHYSICAL AND INORGANIC CHEMISTRY, SECOND EDITION, BY WILLIAM A.

TILDEN, D.Sc., F.R.S. LONDON: J. AND A. CHURCHILL.

IN this edition we welcome the appearance of what is really the fourteenth edition of our old friend "Fownes," from the pages of which most of our living chemists have received their primary instruction. The new Editor has done his part in a very careful manner and has succeeded in bringing the work up to date without any undue increase in size. Another feature for which he is responsible is the doing away with the separate introductory physical part and the scattering of the same through the text. In this way, when it is necessary to refer to any physical point in connection with the chemical subject in hand, the matter in question is then and there fully explained. Of course no chemical book is quite free from printers' errors, and when they occur in this edition they are sufficiently glaring, as for example, when we are told upon page 9 that "3HCl or (HCl), denotes 2 molecules of hydrogen chloride." Taking, however, the book as a whole, there is really no other work extant that occupies so useful a middle place between the cram book and the great works of reference as does this work, of which it might be said that authors come and go but "Fownes" goes on for ever.

# THE ANALYST.

MARCH, 1890.

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### PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

AN ordinary meeting of the Society was held at Burlington House, on the 12th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

The following gentlemen were proposed for election as members: Robert Hellon, Ph.D., Public Analyst for Cumberland, and J. B. Harrison, of British Guiana.

The following papers were read:—

"On the Composition of Milk and Milk Products."—By DR. P. VIETH.

"On the Detection of Methylated Sweet Spirits of Nitre."—By DR. MUTER.

"On the Detection of Cotton Seed Oil in Lard."—By DR. MUTER AND L. DE KONINGH.

"On the Solubility of Phosphate of Alumina in Acetic Acid, with special reference to the extraction of Alumina from Flour, Bread, etc."—By W. C. YOUNG.

A paper by Dr. Muter "On the Analysis of Disinfecting Powders Containing Commercial Carbolic and Sulphurous Acid," was deferred till next meeting.

The next meeting will be held at Burlington House, on Wednesday, the 12th inst. :

# THE ANALYSIS OF MEDICINES DISPENSED FROM PHYSICIANS' PRESCRIPTIONS: A RAPID METHOD OF ESTIMATING QUININE IN MEDICINE.

BY DR. SEATON AND MR. H. DROOP RICHMOND.

*(Read at the Meeting, January, 1890.)*

THE analysis of medicines dispensed from physicians' prescriptions is a part of the work of a public analyst which has not, as yet, received the amount of attention it deserves. This seeming neglect is due to several causes, the chief of which seems to be the difficulty in obtaining the effective combination of the several persons whose combined action is required. To procure a sample of medicine which may be submitted to the public analyst under the Food and Drugs Adulteration Act, it is necessary, first of all, that the inspector appointed under the Act should in this particular, be under the immediate guidance of the Medical Officer of Health; then a physician's prescription (clearly written) must be obtained, which is suitable for analysis; and thirdly, the sample when obtained under the provisions of the Act, must be submitted to the Public Analyst, who very frequently has no immediate communication either with the authority whom he serves or its officers. In writing a prescription for the purpose of obtaining a sample of medicine for analysis, regard must be had not only to the suitability of the drug—simple or combined, from the analytical point of view—but to its exhibition in forms or doses usually prescribed by English practitioners in medicines. For example, if an inspector were to present a prescription for a quinine mixture containing more than 2 to 5 grains in a dose, the attention of the dispenser would immediately be directed to the unusual character of the prescription, and consequently more than usual care would be taken in the dispensing of the medicine. In taking the sample under the Act the inspector has to divide the medicine into three parts, and consequently the amount of the drug present in the third part submitted to the Public Analyst is frequently very small.

A not uncommon prescription for a quinine mixture is as follows:—

Quininae sulphatis, gr. xii.

Acid : sulph : dil.  $\text{m}$  xx.

Aquae destillatae,  $\text{z}$  viii.

Here the amount of the drug present in a third part of the medicine is only 4 grains of the sulphate (the alkaloid being, of course, still less), so that the operation of analysis must be very delicate if errors in dispensing of such amounts as 10 per cent. or 20 per cent. are to be estimated. Our late President, Mr. Allen, was the first to take up this subject. His action must have produced a good effect, not only in the neighbourhood of Sheffield, but throughout a far wider sphere. In discussing some of the results of Mr. Allen's work, Dr. Dupré remarked that his own experience showed that a considerable amount of adulteration was practised in relation to drugs and medicines—that is to say, if the leaving out of an appreciable proportion of the active agent is to be considered adulteration. Most certainly it is, and we would further say that the *adding* of an appreciable proportion of the active agent would, we believe, be considered an adulteration. A short time since we had occasion to analyse three samples of medicines containing bromide of potassium as the active agent. In one sample we found that the amount present exceeded the amount prescribed by 25 per cent., and we have no doubt

that if this case could have been the subject of magisterial proceedings a conviction would have been obtained.

But to return to Mr. Allen's investigations. We find on the 19th page of *THE ANALYST*, Vol. 1, a paper on the determination of quinine by the ammonia and ether process, which is generally pursued, but which is a lengthy and difficult process even when carried out by the modification suggested by Mr. Wynter Blyth. It also necessitates the use of an expensive reagent, viz., ether. These objections to the general adoption of the ammonia and ether process have led us to the suggestion of the following method, which we have found to be perfectly reliable within certain limits, and which has the advantage of being rapid and inexpensive. We do not recommend it in substitution of the ammonia and ether process, as the final method of determining the proportion of quinine in medicine, but as a preliminary process which will enable the analyst to decide whether an error in dispensing has been committed, sufficient in extent to bring the case within the scope of the Adulteration Act. We have found that quinine bisulphate is neutral to methyl orange, while the base itself has no action on phenol phthalein; and we have, bearing these facts in mind, adapted to the determination of quinine the method of alkalimetry. We prefer to operate as follows:—

To 25 c.c. of medicine add 2 drops of methyl orange ( $\cdot 25$  grm. in one litre of water), and 2 drops of phenol phthalein ( $\cdot 5$  grm. in one litre of 50 per cent. alcohol), titrate with  $\frac{N}{10}$  Baryta solution until the free acid is all neutralised, which is shown by the red colour just changing to a brown. Note the number of c.c. used. Continue titration until the pink colour of the phenol phthalein appears. Care must be taken not to overstep this last point, as the colour does not develop quite immediately. The difference between the two titrations, multiplied by the factor  $\cdot 0218$ , gives the weight of the quinine sulphate (*i.e.*, the 7-molecule of water hydrate) in grms. in the 25 c.c. The number of c.c. in the medicine prescribed is known, and the calculation becomes a simple proportion sum.

The method is, of course, not applicable in the presence of salts, of which the base is precipitated by Baryta.

The following is the result of the estimation of quinine in the same medicines by the volumetric and gravimetric processes respectively. Four samples of medicine were obtained in the usual way, and it will be seen that the results of the two methods closely correspond:—

|    |    |    | Volumetric. | Gravimetric. |
|----|----|----|-------------|--------------|
| 1. | .. | .. | 21.2        | 20.8         |
| 2. | .. | .. | 23.4        | 23.2         |
| 3. | .. | .. | 16.5        | 16.1         |
| 4. | .. | .. | 20.3        | 20.0         |

We have further tested the process in the following way: Solutions of quinine, accurately prepared, were obtained by one of us from Messrs. Bell and Co. Solution A contained 12 grains by weight of Howard's quinine sulphate; solution B, 20 grains; solution C, 18 grains; and solution D, 15 grains. Four samples of each solution were obtained, and they were submitted to the other for estimation by our process.

The process gave the following results:—

|                                |    |      |      |      |      |
|--------------------------------|----|------|------|------|------|
| A. (12 gr.) found respectively | .. | 12.1 | 12.2 | 11.8 | 12.0 |
| B. (20 gr.)                    | .. | 19.7 | 19.9 | 19.9 | 19.7 |
| C. (18 gr.)                    | .. | 17.5 | 17.6 | 17.5 | 17.8 |
| D. (15 gr.)                    | .. | 15.4 | 14.7 | 14.9 | 15.2 |



## ON THE COMPOSITION OF MILK AND MILK PRODUCTS.

By DR. P. VIETH.

*(Read at Meeting, February, 1890.)*

THE kind reception which you have accorded to former communications of a similar kind (see THE ANALYST, VII. p. 53; VIII. p. 33; IX. p. 56; X. p. 67; XI. p. 66; XII. p. 39; XIII. p. 46; and XIV. p. 69) encourages me to lay before you to-night what perhaps might be best described as "a report on the work done in the laboratory, which is under my charge, during the year 1889."

The fact that the work is carried on from year to year under similar conditions, and with the same objects in view, makes it impossible to avoid in these annual reports a certain uniformity of outside appearance and repetitions with regard to their contents. When first brought before the Society, these reports were considered not without value, and I contend that their continuation cannot deduct from their value, although it may make them less attractive.

The total number of samples submitted to analytical examination during the past year is 22,728, viz.:—

|                         |   |   |  |
|-------------------------|---|---|--|
| 20,674 samples of milk, |   |   |  |
| 1,123                   | „ | cream,                                      |  |
| 609                     | „ | skim milk,                                  |  |
| 29                      | „ | buttermilk,                                 |  |
| 231                     | „ | butter and butter-fat,                      |  |
| 12                      | „ | milk preparations for infants and invalids, |  |
| 42                      | „ | water,                                      |  |
| 8                       | „ | sundry articles.                            |  |

Of the milk samples, 12,617 were taken from the railway churns on their arrival in the dairy, 1,757 from the milk before being sent out, 2,623 by the inspectors employed by the business, from the man while distributing the milk, and 324 from the small quantities of milk brought back from the rounds. The following table contains the monthly averages of the results referring to these samples:—

AVERAGE COMPOSITION OF MILK.

| 1889.          | Samples taken. |           |      |              |                  |                  |               |
|----------------|----------------|-----------|------|--------------|------------------|------------------|---------------|
|                | On arrival.    |           |      |              | Before sent out. | During delivery. | From returns. |
|                | Spec. Grvty.   | Tot. Sol. | Fat. | Sol. n. fat. | Tot. Sol.        | Tot. Sol.        | Tot. Sol.     |
| January ..     | 1·0320         | 12·79     | 3·73 | 9·06         | —                | 12·8             | —             |
| February ..    | 1·0321         | 12·76     | 3·70 | 9·06         | —                | 12·7             | —             |
| March ..       | 1·0319         | 12·73     | 3·70 | 9·03         | 12·6             | 12·6             | —             |
| April ..       | 1·0319         | 12·68     | 3·66 | 9·02         | 12·6             | 12·6             | —             |
| May ..         | 1·0322         | 12·67     | 3·60 | 9·07         | 12·6             | 12·6             | —             |
| June ..        | 1·0322         | 12·55     | 3·49 | 9·06         | 12·5             | 12·6             | —             |
| July ..        | 1·0319         | 12·65     | 3·65 | 9·00         | 12·5             | 12·6             | —             |
| August ..      | 1·0320         | 12·77     | 3·72 | 9·05         | 12·7             | 12·7             | 12·7          |
| September ..   | 1·0321         | 12·91     | 3·80 | 9·11         | 12·8             | 12·9             | 12·8          |
| October ..     | 1·0323         | 13·21     | 4·03 | 9·18         | 13·1             | 13·2             | 13·3          |
| November ..    | 1·0321         | 13·19     | 4·04 | 9·15         | 13·1             | 13·1             | 13·3          |
| December ..    | 1·0322         | 13·02     | 3·88 | 9·14         | 12·9             | 13·0             | 13·0          |
| Yearly average | 1·0321         | 12·83     | 3·75 | 9·08         | —                | 12·8             | —             |

It will be seen from this table that the richest milk was, as usual, received during the latter part of the year, while the lowest percentages of total solids and fat were observed in the month of June. I attribute the somewhat exceptional quality of the milk received in June—the lowest monthly average observed since the last five years—to the extraordinary atmospheric conditions, to wit, the long spell of warm and dry weather which reigned in May and June. The agreement between the several sets of samples is satisfactory, considering that not much time is allowed for mixing the milk and drawing the samples.

There were further analysed, 1,814 samples of milk, yielded by individual cows. An investigation regarding the composition of milk of individual cows was commenced in April, 1887, and up to the end of last year about 5,000 samples of such milk have been submitted to analysis. It is my intention to bring the results of this investigation under your notice as soon as I shall find the time to work the vast material into a suitable shape.

Cream samples were taken before the cream was sent out, and also while it was delivered to the customers; 412 samples of the former and 303 samples of the latter kind having been analysed with the following results:—

## AVERAGE PERCENTAGE OF FAT IN CREAM.

| 1889.                  | Samples taken.   |                  |
|------------------------|------------------|------------------|
|                        | Before sent out. | During delivery. |
| January .. .. .        | 46.5             | 47.0             |
| February .. .. .       | 46.8             | 47.4             |
| March .. .. .          | 47.2             | 47.6             |
| April .. .. .          | 49.4             | 48.9             |
| May .. .. .            | 49.5             | 49.9             |
| June .. .. .           | 48.2             | 48.0             |
| July .. .. .           | 45.6             | 45.5             |
| August .. .. .         | 45.6             | 45.7             |
| September .. .. .      | 45.6             | 45.8             |
| October .. .. .        | 47.9             | 47.5             |
| November .. .. .       | 48.3             | 48.9             |
| December .. .. .       | 46.8             | 46.8             |
| Yearly average .. .. . | 47.3             | 47.4             |

I have mentioned on former occasions that an absolute agreement between the two sets of samples of cream cannot be expected for two reasons; firstly, because samples taken before distribution refer to morning and afternoon delivery, while samples taken during distribution refer to afternoon delivery only, the cream being left in sealed cans in the morning; and secondly, because there is some difficulty of getting fair average samples from large bulks of cream. Keeping this in mind, I believe the agreement between the two series of analysis is all that can be expected.

The composition of fifty-one samples of clotted cream was as follows :—

|                |    |    |                |               |           |
|----------------|----|----|----------------|---------------|-----------|
| Total solids   | .. | .. | 54.99 to 69.05 | average 63.31 | per cent. |
| Fat            | .. | .. | 47.72 „ 62.83  | „ 56.69       | „ „       |
| Solids not fat | .. | .. | 5.37 „ 8.47    | „ 6.62        | „ „       |
| Ash            | .. | .. | .44 „ .65      | „ .53         | „ „       |

I wish, in this place, to draw once more attention to a fact which I have mentioned on several previous occasions, viz., to the close relationship existing in normal milks and creams between the total amount of non-fatty solids and the amount of mineral matter, or ash, contained therein. I have invariably found the ash to amount to, as near as possible, 8 per cent. of the non-fatty solids, and look at this fact not only as a very useful check on the analysis, but also as a proof of the normal quality of a milk.

The 104 samples of butter analysed were of different origin ; they may be classed as English, French, Danish and Swedish, and German. Their composition was as follows :—

BUTTER CHURNED IN LONDON, FRESH AND SALT.

|                        |      |        |                |                     |           |
|------------------------|------|--------|----------------|---------------------|-----------|
| Fat                    | ..   | ..     | 85.62 to 90.49 | average 87.13       | per cent. |
| Water                  | ..   | ..     | 8.03 „ 13.48   | „ 11.55             | „ „       |
| Solids not fat         | ..   | ..     | .63 „ 2.83     | „ 1.32              | „ „       |
| Chlorides, as NaCl     | ..   | ..     | .38 „ 2.44     | „ .96               | „ „       |
| Volatile acids, Wollny | 25.8 | „ 29.2 | „ 26.9         | c.c. $\frac{n}{10}$ | alk.      |

FRENCH BUTTER, FRESH.

|                        |      |        |                |                     |           |
|------------------------|------|--------|----------------|---------------------|-----------|
| Fat                    | ..   | ..     | 83.74 to 85.62 | average 84.78       | per cent. |
| Water                  | ..   | ..     | 13.22 „ 14.44  | „ 13.80             | „ „       |
| Solids not fat         | ..   | ..     | 1.00 „ 2.00    | „ 1.42              | „ „       |
| Chlorides, as NaCl     | ..   | ..     | .05 „ .17      | „ .08               | „ „       |
| Volatile acids, Wollny | 26.7 | „ 30.5 | „ 28.9         | c.c. $\frac{n}{10}$ | alk.      |

DANISH AND SWEDISH BUTTER, SALT.

|                        |      |        |                |                     |           |
|------------------------|------|--------|----------------|---------------------|-----------|
| Fat                    | ..   | ..     | 78.91 to 85.61 | average 82.84       | per cent. |
| Water                  | ..   | ..     | 11.86 „ 16.96  | „ 13.75             | „ „       |
| Solids not fat         | ..   | ..     | 2.21 „ 4.70    | „ 3.41              | „ „       |
| Chlorides, as NaCl     | ..   | ..     | 1.06 „ 3.00    | „ 2.07              | „ „       |
| Volatile acids, Wollny | 27.2 | „ 29.8 | „ 28.3         | c.c. $\frac{n}{10}$ | alk.      |

KIEL BUTTER, SALT.

|                        |      |        |                |                     |           |
|------------------------|------|--------|----------------|---------------------|-----------|
| Fat                    | ..   | ..     | 82.00 to 89.45 | average 86.04       | per cent. |
| Water                  | ..   | ..     | 8.39 „ 15.23   | „ 11.56             | „ „       |
| Solids not fat         | ..   | ..     | 1.70 „ 2.89    | „ 2.40              | „ „       |
| Chlorides, as NaCl     | ..   | ..     | .84 „ 1.81     | „ 1.29              | „ „       |
| Volatile acids, Wollny | 21.1 | „ 29.8 | „ 26.5         | c.c. $\frac{n}{10}$ | alk.      |

The volatile acids were also determined in 127 samples of butter-fat prepared from small quantities of either milk or cream in the laboratory. The majority of the results of these determinations were embodied in a paper which I had the honour of submitting to the Society at the meeting in June.

Some pure butter-fat which had been exposed to the action of air and light for one year and nine months, had become quite white. It had been analysed when fresh, and was re-analysed in its bleached condition. The following are the results :—

| Fresh.   | Bleached.  |
|--|--|
| Insoluble acids, Hehner 87.72 per cent.                | Insoluble acids, Hehner 83.82 per cent.              |
| Volatile acids, Reichert 15.0 c.c. $\frac{n}{10}$ alk. | Volatile acids, Wollny 31.7 c.c. $\frac{n}{10}$ alk. |

It appears, then, that the insoluble fatty acids decreased at the ratio of 100 to 95.5, while the volatile fatty acids (Reichert's figure doubled) increased at the ratio of 94.6 to 100. The soap and also the insoluble acids were, in the case of the bleached sample, of dark, red-brown colour.

I believe I am right in saying that I have almost every year met with at least one new milk preservative, or rather, with a milk preservative under a new name, for they all have that in common, that they contain as active principle boracic acid in some form or other. "Dr. Beesly's Antiseptic Milk Preservative," which came under my notice last year, proved to be no exception to the rule.

#### DISCUSSION.

DR. MUTER said it seemed to him that they all ought to be grateful to Dr. VIETH for giving them those figures, because it was the sort of work which enables them to fix accurate limits for things. Curious points often came out, such as that about the relation between solids not fat and ash, a striking matter which could only be discovered by a very large number of analyses being made by one person.

MR. ALLEN asked if Dr. Vieth could guarantee the genuine nature of the exceptional butters to which he referred in his paper.

DR. VIETH, in reply, said he could not guarantee the purity of the Kiel butters not having seen them made himself, but he had not the slightest doubt they were perfectly genuine. The butters came over in casks.

MR. HEUNER asked Dr. Vieth whether it was not a fact that the butter prices had risen at the same time that the volatile acids in Dr. Vieth's samples had declined. He thought that unless the origin of exceptional samples was thoroughly authenticated they should not too readily give evidence to alleged exceptions. He had noticed that soon after the reading of Mr. Allen's paper on the exceptional Danish butters, a great proportion of all butter samples analysed by him had disclosed volatile fatty acids. The foreign shippers of butter knew well how to take advantage of these exceptional samples. Mr. Hehner related several cases from his own experience, which showed that these shippers were now mixing from 10 to 15 per cent. of margarine with butter, in the confident belief that they could not be detected.

MR. ESTCOURT, whilst thanking Dr. Vieth for his valuable paper, said he agreed with Mr. Hehner in his remarks as to the Kiel samples. Mr. Allen had said that these results were not discussable. They certainly did not compare with the Danish and Swedish, which averaged 28 per cent., but he was going to mention a case in which Mr. Allen was himself concerned at a time when mixtures were not supposed to exist. Mr. Allen had the official sample, and he the sample of the vendor.

He agreed with Mr. Allen in pronouncing it to be a mixture.

His clients then came to him and disclosed the name of the Irish firm who sold it them, and it was found that the Irish firm had really been manufacturing this margarine by adding foreign fat to last year's well-washed butter.

He saw the certificate of Dr. Tichborne, of Dublin, stated to be of the same butter, which was also stated to have passed Somerset House. This was given to each purchaser, but the certificates of Mr. Allen and himself put an end to this manufacture, fortunately before Mr. Allen adopted so low a standard as of recent time.

It was quite certain that if they accepted Dr. Vieth's figures, 25 per cent. foreign fat might pass, and they would descend to a lower depth than that.

MR. CASSAL agreed with Mr. Hehner, in thinking that credence was too readily given to these exceptional cases. The position of a public analyst, called upon to make official examinations of butter coming from entirely unknown sources, was, however, very often a difficult one, and it was obvious that the greatest caution should be observed

in certifying to small percentages of adulteration. It should be remembered that the average magistrate played a considerable part in prosecutions under the Acts; but more effectual steps might, nevertheless, be taken to check systematic "small" adulteration.

DR. VIETH, in reply, said the public analyst ought to look at his office from two points of view. While trying to detect adulteration and thus helping to bring offenders to law, he should also think it his duty to protect innocent people. There was no doubt that abnormal butters did exist; these were abnormal samples. Low results had been found in genuine Swedish and Danish butters; they had also been observed in Italy. From a paper of Mr. Allen's, they would remember that Professor Stein in Copenhagen was able to point with his finger to dairies where abnormal butters might be, and indeed were found. He did not think that Mr. Hohner would doubt that genuine butters with abnormally low volatile acids did exist.

### A SIMPLE METHOD OF DETECTING THE PRESENCE OF METHYLATED SWEET SPIRIT OF NITRE.

By JOHN MUTER, Ph.D., F.R.S.E.

*Read at Meeting, February, 1890.*

I HAVE never yet met with a really simple test for this fraudulent article mentioned in any print. There is, at the present time a great amount of it about, and it behoves us all to be on the alert to stop it. From what I have seen, the regularly licensed chemists and druggists do not patronise the makers of the article to any great extent, but it chiefly finds its way to cutting stores and oilmen, who undersell the pharmacist in all his articles not included in the poisons schedule. It can, of course, be made of correct specific gravity and to yield the right amount of nitric oxide by the B.P. test, and yet sold at a splendid profit. There ought, certainly, to be introduced into the next B.P. some simple method whereby the stuff can be readily found out in a few moments; and in the hope that this will be done, I beg to submit the following perfectly simple, yet, so far as I know, entirely reliable test. At least, among no end of samples, I have never yet failed with it. The test simply consists in putting some of the sample into a glass, with a lump of solid caustic potash (about the size of a small bean), and stirring till nearly dissolved. Real B.P. spirit, made from rectified spirit of B. P. quality (which it ought to be, or it is not a legal tender as B.P. spirit) will lose all its odour of nitrous ether, and, after standing for half-an-hour, will not have become darker than the very palest tint of straw-colour (not visible by gas-light), and it will then only have the odour of plain rectified spirit. The methylated article, on the other hand, will become of a dark colour, varying from deep yellow to orange red, and will give off the well-known odour of methylated spirit in all its nakedness. Should any farther confirmation be required, then we may have recourse to the old "Miller" process, or we may distill off some of the potashed spirit, and put 10 grams. of it in the dark for 48 hours, with a good excess of Hübl's solution. The genuine B.P. spirit has never, in my hands, absorbed any iodine, while the methylated article takes up from .4 to .7 per cent. of iodine, according to the quality of the spirit employed. There is, however, no need to trouble about this, because the simple combined observation of the odour and colour after potash are perfectly convincing.

### NOTE ON THE ANALYSIS OF LARD, COTTON OIL, TALLOW, ETC.

By JOHN MUTER, Ph.D., F.R.S.E., AND L. DE KONINGH, F.I.C

*Read at Meeting, February, 1890.*

In the month of February, 1889,\* we proposed an improved method for the volumetric estimation of oleic acid in fats and oils, and of subsequently applying Hübl's iodine

\* See ANALYST for April, 1889.

absorption test to the acid thus liberated, without its having been exposed to heat or to any influence likely to be prejudicial to the accuracy of the iodine number thereby obtained. We feared that the calls of our ordinary business would make it a very tedious matter for us to examine all the common fats and oils, and to suggest standards based upon the process, and we therefore invited our colleagues to give us their co-operation with this object. In the meantime we have been applying it to the current matters that have turned up, and especially to the analysis of lard, and we now give the standards we have adopted in this matter.

1. *Tallow*.—The oleic acid isolated from tallow seems to us to be practically pure oleic acid. In many experiments we have made, we generally get from .1 to .2 per cent. from theory. Tallow is therefore, in our opinion, the best source from which to prepare perfectly pure oleic acid, giving an iodine number of 90.

2. *Lard*.—Although it would be unwarrantable to jump to the conclusion that this fat contains acids of the linoleic series, still we have not as yet met with any sample which gives an acid having as low an iodine absorbing power as the oleic acid from tallow. After careful study of many samples we propose to put the iodine number of the oleic acid from lard at 93, but not to condemn under 94.

3. *Cotton Oil*.—This oil being often subjected to a good deal of chemical treatment before it is sold, it would not be a matter of surprise if the iodine number of its oleic acid should be subject to a good deal of variation. However, in all the samples we have as yet tested, we do not find any very great difference, and we propose to put the iodine figure of the cotton oleic acid at 135.

We are not aware that any of our English colleagues have taken up the process, but it has attracted some notice abroad, and just as we are writing, we have received a copy of a paper communicated to the Hungarian Academy of Sciences by Dr. Alex. von Asboth, in which he gives a very favourable criticism of our process, and proposes to fix the iodine numbers of the fluid acids of lard and cotton oil respectively at 94 and 136. Dr. Asboth thus gets the same calculation difference between these two fats as we do, although he is one degree higher than us in both cases, which may after all be only a matter of the "personal equation" in working.

As regards the application of the process it may be interesting to extract two of our experiments on known mixtures, so as to show both the mode of calculating and the degree of accuracy that may fairly be expected in practice.

*Experiment A*.—This was made on a mixture of 43 per cent. of lard and 57 of cotton oil. The sample yielded 64 per cent. of fluid acids, and these acids gave an iodine absorption figure of 118 (lard 93, and cotton oil 135). Therefore  $(135-93) : (118-93) :: 64 : x, x = 38$  cotton oleic acid. As we may take common cotton oil to contain about 70 per cent. of liquid acids, we get  $70 : 100 :: 38 : x, x = 54$  per cent. of adulteration in the sample.

*Experiment B*.—Made on a mixture containing 75 per cent. of lard and 25 of cotton oil. Found 58 per cent. of liquid acids which gave an iodine number of 103. Therefore:— $(135-93) : (103-93) :: 58 : x, x = 14$  per cent. of cotton oil acids. Then as  $70 : 100 :: 14 : x, x = 20$  per cent. of adulteration.

It will be seen that, like all such processes based upon average standards, the

accuracy diminishes as the adulteration gets smaller, and if the latter is below 10 per cent. then the process is only really of qualitative value. However, we agree with von Asboth in saying that any lard the acids of which show a greater iodine absorption than 94, must be looked upon with the gravest suspicion. One thing is certain, namely, that the true imitation lard which, if properly made, can defeat the ordinary iodine test, will not escape detection if treated by our method. The only fat which, if introduced in a judicious quantity, might upset our process is cocoanut oil. This oil contains very little olein, but still yields a fair proportion of acids (chiefly caproic) which also form lead salts that are at once insoluble in water and soluble in ether. Before our process can be applied, it is therefore necessary to remove these acids, and although our investigations on this subject are not yet complete, we believe that the best way to accomplish this will be to heat the apparent oleic acid (obtained by evaporation of the ether) in a current of carbon dioxide at a temperature of  $110^{\circ}$  to  $115^{\circ}$  C. until all the interfering acids are removed. After this is done, the remaining acids are to be weighed and "Hubled." The presence of cocoanut fat is so readily detected qualitatively, that no analyst would have any difficulty in condemning a sample containing it, so it is not probable that its use will be resorted to.

We have placed upon the table one of "Muter's olein tubes" as now manufactured in Germany, and which are readily procurable through Messrs. Baird and Tatlock, of Glasgow, or indeed of any similar house.

#### DISCUSSION.

MR. ALLEN said they were much indebted to DR. MUTER for this continuation of his former very important paper. The process was really one likely to throw light upon the unknown characters of these fatty acids, which rendered it extremely valuable. The constitution of these acids had been up till now ignored by chemists who had too long classed them as being all stearic, palmitic, and oleic. What they had been in the habit of calling oleic acid was by no means of such a constant character as they had been assuming. It was by highly refined researches and methods depending on the constitution of the fatty acids that they could hope to differentiate them and detect the oils of which they were constituents. It was to methods like that of Dr. Muter's and those of Hazura and other recent investigators that they might hope to detect vegetable oils in butter and lard.

*(Conclusion of the Society's Proceedings.)*

#### NOTE ON THE PURIFICATION OF ALCOHOL FOR LABORATORY USES

By E. WALLER, PH. D.

COMPARATIVELY recently several papers have appeared on the subject of the reactions of potassium permanganate with alcohols, and the impurities which they may contain.\*

In preparing alcoholic solutions of caustic alkalies, and also of silver nitrate (for fat tests, etc.), I have been annoyed, as have other chemists, by the unsatisfactory character of the solutions obtained in consequence of the presence of impurities in the alcohol bought for laboratory use. I find also that most alcohol of 93 per cent. when kept in tin cans slowly reacts on the tin, giving after a while a cloud of  $\text{SnO}_2$ , which is too fine

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\* Habermann. *Frs. Ztschr. anal. Chem.* 27, 663. Reese, *ib.* 28, 355.  
Ca encuve. *Bull. Soc. Chim. (Paris)* [3] 1, 700. See also *Dingl. Polyt. Jour.*, 273, 374.

to filter out, and renders purification by distillation necessary. In the light of the results obtained by the writers above alluded to, I have adopted the following method for the purification of my alcohol, on which I ask the criticism of the members of the society :—

A convenient amount of the alcohol to be purified is shaken with pulverised potassium permanganate until it assumes a decided colour. It is then allowed to stand for some hours, until the permanganate has been decomposed and brown manganese oxide is deposited. A pinch of pulverised calcium carbonate is then added, and the alcohol distilled at the rate of about 50 c. cm. in twenty minutes from a flask provided with a Wurz tube or one of the Lebel-Heninger pattern. The distillate is tested frequently until about 10 c. cm. thereof, when boiled with 1 c. cm. of strong (syrup) solution of caustic soda or potash, gives no perceptible yellow colouration on standing for twenty minutes or half an hour. What distils over after that time is preserved for use.

The first distillates may be added to the small amount remaining in the distilling flask (which should not be driven down to complete dryness), and a fresh portion of purified alcohol recovered.

The rationale of the proceeding appears to be that the permanganate oxidises and destroys chiefly the fusel-oil, furfural and other compounds of that nature, the acids resulting from the reaction are neutralised by the calcium carbonate added before distillation, and by distilling slowly the aldehyde at least is concentrated in the first portions of the distillate. Distillation of alcohol containing caustic potash or soda seemed to cause a constant formation of aldehyde. The alcohol thus purified is perfectly neutral, and gives most satisfactory results when used as a solvent for caustic alkalies or silver nitrate, the solutions remaining as colourless as distilled water, even after boiling and standing indefinitely, if properly protected from dust and other external influences.—*Jour. Am. Chem. Soc.*

#### TEST FOR COTTON-SEED OIL IN LARD.

By FRANK P. PERKINS, F.I.C.

The following may be useful in *sorting* samples of lard which have to be examined for cotton-seed oil.

I find that if a little powdered potassium dichromate—about .02 to .03 gramme—be mixed with a few drops of concentrated sulphuric acid in a porcelain dish, and a small portion—about .5 gramme—of the suspected sample be then introduced, on stirring well a second time, adding water, and stirring again, there will in the presence of cotton-seed oil be developed a green colour, due to the change of chromic acid to chromic oxide, but if the vegetable oil be absent the yellow colour of the dichromate will still prevail. The colour should not be judged until water has been added, and the mixture stirred for some seconds.

This test I have tried with samples of bladder lard, with American lard known to be adulterated, with purely rendered home lard, the same containing a certain proportion of cotton-seed oil, and with cotton-seed oil itself. It has not failed to detect the cotton-seed oil either alone or when mixed with lard. How the test is affected by other vegetable oils I have not yet determined, I therefore submit it with diffidence, and should be glad to know how it answers in the hands of other experimenters.



## ON THE BEHAVIOUR OF PHENOL-PHTHALEIN WITH AMMONIA.

By J. H. LONG.

*(Concluded.)*

In another series of experiments, ammonia was run into the solution containing hydrochloric acid and different amounts of the phenol-phthalein. Where but a few drops of this were taken, the end reaction could not be observed accurately; with larger amounts the reaction was sharper, but only came after addition of an excess of alkali.

1. With 25 c.c. of acid and 5 c.c. of indicator I used 25.57 c.c. of  $\text{NH}_4\text{OH}$ .

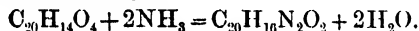
2. With 25 c.c. of acid and 10 c.c. of indicator I used 25.28 c.c. of  $\text{NH}_4\text{OH}$ .

In presence of alcohol the reaction was always less distinct than with water, and more alkali was required to bring it.

The above results seem to indicate that ammonia combines with phenol-phthalein, forming, to some extent, a colourless compound, besides forming a coloured one as does sodium hydrate; and also that this colourless body is produced more quickly as the temperature is higher or the ammonia stronger.

I expressed the opinion in my former paper, referred to above, that the phenol-di-imido-phthalein discovered by Baeyer is the compound formed here, and that this explains the peculiar reaction.

The experiments given below seem to confirm fully this view. Baeyer\* states that phenol-phthalein and aqueous ammonia heated to  $160^\circ$ – $170^\circ$  in sealed tubes for some hours react on each other in this way:—



The phenol-di-imido-phthalein is a colourless body soluble in alkalis without colour, but which dissolves at a high temperature in acids with formation of an ammonium salt and phenol-phthalein:—



I prepared the product by the following methods:—

1. 3 grms. of phenol-phthalein and 30 c.c. of strong ammonia were heated during three hours in a sealed tube to  $160^\circ$  C. The tube was then opened and the contents neutralised with hydrochloric acid. This precipitated a gummy mass, which was washed thoroughly with water, and finally dissolved in 90 per cent. alcohol. The solution, after filtration through bone charcoal, was evaporated to dryness. The residue left was dissolved in a mixture of equal parts of benzene and alcohol. The solution was allowed to evaporate spontaneously, leaving a residue, which was heated to  $120^\circ$  C. to completely remove all traces of the solvent. The product then remained as a colourless mass of fine needle-shaped crystals.

2. 10 grms. of phenol-phthalein were treated with 200 c.c. of strong ammonia solution in a flask kept hot on a water-bath during fifteen hours; at the end of that time the solution was neutralised with hydrochloric acid, and an insoluble gummy mass formed was treated as under 1.

3. 10 grms. of phenol-phthalein were dissolved in 200 c.c. of strong ammonia water (26 per cent.) at the ordinary temperature of the room. The colour formed at

\* Ber. d. chem. Gessell. 11, 1297.

first disappeared in four days without application of heat. I then neutralised with hydrochloric acid, and obtained the same product as above, which was treated in the same manner.

The three substances so obtained appeared quite similar, and turned red when moderately heated in a porcelain dish, melting finally at a higher temperature. They dissolved in sodium hydroxide solution without colour. When heated to  $110^{\circ}\text{C}$ . with hydrochloric acid they formed ammonium chloride and phenol-phthalein, as shown by various tests. They all dissolved in strong nitric acid with a marked yellow colour, which disappeared on addition of alkali.

It is apparent, therefore, that the phenol-di-imido-phthalein can be formed at ordinary temperature as well as in a sealed tube at  $160^{\circ}$ , although the preparation of a large amount at the lower temperature would require a much longer time.

The combination between the free alkali and the trace used as indicator in a practical titration would naturally require but a very short time at the ordinary temperature.

The rapidity of liberation of ammonia from an ammonium salt by fixed alkali depends on the temperature, and hence the very slight disturbance of the reaction with the mixed solutions in the above experiments carried out at a low temperature. Addition of sodium hydroxide seems to aid the reaction with ammonia solution, as shown by experiments in which I added the phenol-phthalein to ammonia solution and then the sodium hydroxide from a burette. With half-normal solutions the colour was lost in half an hour by mixing 25 c.c. sodium hydroxide, 20 c.c. ammonia, and .2 c.c. of the indicator. Similar results were obtained with other solutions.

The above experiments show that the phenol-phthalein can be used with ammonia by taking certain precautions, and they also suggest why the behaviour of this alkali was not sooner recognised. By working at a low temperature with a sufficiently large amount of the indicator, it was shown that fairly sharp results can be obtained. However, as we have other good indicators, it may never seem necessary to take these precautions.

After the introduction of the phenol-phthalein as an indicator, some time elapsed before its extreme sensitiveness was realised, and undoubtedly more was then added to a solution than is now considered necessary. Under these circumstances the difference in behaviour between soda and ammonia would scarcely be noticed, and it remained for later observers, working with less of the reagent, to detect the discrepancy.

I am greatly indebted to my assistant, Mr. Mark Powers, for help in the details of the above experiments.

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#### REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

A NEW METHOD FOR THE ESTIMATION OF NICOTINE. MAX POPOVICH (*Journ. de Ph. et de chim.*, p. 215).—By the advice of Professor Kossell, the author has set himself to study whether the polariscope can be satisfactorily employed for the estimation of nicotine. Pure nicotine is known to be levogyrate, and its rotatory power  $A_D$ ,— $161^{\circ}5$ . In an alcoholic or watery solution this rotatory power diminishes. Thus in a mixture of

nicotine and water containing 10 per cent. of water, it is only  $133^{\circ}8$ . In spite of these variations, M. Popovice has succeeded in successfully estimating the nicotine in tobacco with sufficient accuracy for ordinary purposes. The author employs Kissling's process for extracting the nicotine from the tobacco as follows:—20 to 40 grammes of powdered tobacco, according to quality, are moistened with 10 c.c. of an alcoholic solution of soda in proof spirit of 6 per cent. strength. After standing for some time, the powder is placed in a Soxhlet's apparatus and continuously extracted with ether for three or four hours. The resulting ethereal solution is treated with 10 c.c. of a solution of a sodium phosphomolybdate in nitric acid, which causes the precipitation of the impure alkaloid. When this precipitate has settled, the ethereal solution is carefully poured off, and distilled water is added to the precipitate in the flask until the contents exactly measure 50 c.c. Eight grammes of finely-powdered barium hydrate are then added to liberate the nicotine, and the whole is allowed to stand for several hours with occasional shaking. The contents of the flask are then filtered, and the alkaline filtrate containing the free nicotine is examined by the polariscope. To provide for the variable rotatory power of nicotine already referred to, the author prepared fifteen ethereal solutions of the pure alkaloid, containing proportions comprised between 0.25 and 2.00 grammes of nicotine in 50 c.c. He treated these exactly as above directed, and then examined the alkaline filtrate in a tube two decimetres long. By this means he constructed the following table:—

| Nicotine contained in<br>50 cent. cubes. | Rotation in minutes. | Weight of nicotine corres-<br>ponding to 1 minute. |
|--|----------------------|--|
| 2,000                                    | 337                  |  |
| 1,875                                    | 318                  | 0.00658  |
| 1,750                                    | 298                  | 0.00625  |
| 1,625                                    | 278                  | —  |
| 1,500                                    | 258                  | —  |
| 1,375                                    | 238                  | —  |
| 1,250                                    | 217                  | 0.00595  |
| 1,225                                    | 196                  | —  |
| 1,000                                    | 175                  | —  |
| 0.875                                    | 154                  | —  |
| 0.750                                    | 133                  | —  |
| 0.625                                    | 111                  | 0.00569  |
| 0.500                                    | 89                   | —  |
| 0.375                                    | 67                   | —  |
| 0.250                                    | 45                   | —  |

If, therefore, in an analysis of tobacco we find a rotation somewhere between 337 and 45 minutes, we can obtain the proportion of nicotine by multiplying the number of minutes by the corresponding factor given in the third column. The process is evidently only reliable when exactly followed in every detail. The author has tested it side by side with Kissling's process on a large number of samples, and has found the results to be concordant.

M. S. A. M.

PREPARATION OF OXYGEN FOR ANALYTICAL PURPOSES IN A KIPP'S APPARATUS. A. BAUMANN (*Zeitschr. f. angew. Chemie*, No. 3, 1890).—To prepare oxygen in a Kipp's apparatus, Neumann recommended a mixture of black oxide of manganese, barium dioxide, and plaster, which is made into cubes, and evolves oxygen when decomposed

with dilute hydrochloric acid. The gas, however, is not pure, but contains chlorine; so it has to be passed through a wash-bottle containing potash. The author warns against the use of these cubes, as he nearly had a serious accident in his laboratory owing to an explosion taking place when the apparatus, at work, stood too near the light. He also does not recommend Volhard's plan, who decomposes compressed chloride of lime with acid solution of hydrogen peroxide, as the gas is also mixed with much chlorine and carbonic acid. The author now proposes to decompose black oxide of manganese with an acid solution of hydrogen peroxide. A rich ore is chosen and made into small pea-sized lumps, from which any fine powder is removed by means of a sieve. After having put an india-rubber ring in the central bulb of the apparatus, and surrounded it with so much asbestos that no grains of manganese can get into the lower bulb, the central bulb is quite filled with the manganese. Commercial peroxide of hydrogen is now acidified with 150 c.c. of sulphuric acid per litre. The gas is now evolved in the same way as one prepares hydrogen from zinc and sulphuric acid. The oxygen evolved is perfectly pure.

L. DE K.

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SCHEME FOR THE ANALYSIS OF CREOLINE. J. W. GUNNING (*Nederl. Tydschr. v. Pharmacie, etc.*, Nov. 1889).—This disinfectant has become a great favourite on the continent, and is supposed to be harmless. Although chiefly composed of neutral tar oils, these, when the product is diluted with water, get into such an extreme state of division that they possess disinfecting properties. In support of this theory, the fact has been observed that the emulsion soon gets inactive. To get an approximate analysis of the compound, the author operates as follows: The creoline is mixed with petroleum ether of 80° Cent. boiling point. First, the two fluids mix, but on adding more the tar oils dissolve, whilst the resin soap separates, which, after having been washed a few times with petroleum ether, will be found soluble in water. On adding acid the resin separates and may be purified with alcohol, and finally weighed. To identify the resin, its acidity equivalent may be taken. The amount of alkali contained in the article may be done by the usual methods. The acid liquid, from which the resin has separated, may contain a little phenol, which may be recovered by shaking out with ether. The tar oils are recovered by evaporating off the petroleum ether. On cooling, any naphthalene will show. Shaking with water will extract any phenol; soda-ley will extract cresol. Bodies of a basic nature may be shaken out with dilute acids, and extracted from the acid solutions by agitating with alkali and ether.

The residual tar oil is dried over calcium chloride, and further identified by its boiling point.

L. DE K.

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ESTIMATION OF FERRIC OXIDE AND ALUMINA IN NATIVE PHOSPHATES. A. STUTZER (*Zeitschr. f. angew. Chemie*, No. 2, 1890).—The conventional process (see ANALYST, January, 1890) does not yield accurate results, especially as the mixed phosphates of iron and alumina may be contaminated with calcium fluoride or other lime compounds. Besides it is unwarrantable to consider half their weight to be phosphoric anhydride, there being a sensible difference in the molecular weight of the two compounds. Glaser has certainly made an improvement by introducing an alcohol process, but the author

thinks the best plan is to isolate the ferric and aluminic hydrates free from phosphoric acid or other impurities.

Five grams. of native phosphate are boiled with 50 c.c. of hydrochloric acid of 1.12 sp. gr., and diluted with water up to 500 c.c. 100 c.c. (= 1 gram.) are pipetted off, made alkaline with ammonia, and then slightly acidified with acetic acid. The mixed precipitate of ferric and aluminic phosphates is collected on a filter and once washed with water. After draining, the precipitate is rinsed back into the beaker, and treated with 150 c.c. of the ordinary solution of molybdate for about five minutes at a gentle heat. The phosphoric acid now completely separates, and the iron and alumina remain in the solution, from which they may be thrown down by slight excess of ammonia. As the precipitate carries with it small quantities of molybdic acid, it is advisable to redissolve in hydrochloric acid and once more to precipitate with ammonia.

L. DE K.

DETECTION OF THE COLOURING MATTER OF ALKANET ROOT. A. BUJARD AND A. KLINGER (*Zeitschr. f. angew Chemie*, No. 1, 1890).—During an analysis of a quack-medicine, the authors were ordered to investigate the nature of the colouring matter. In the first sample there was not enough colouring matter to make a satisfactory spectroscopic examination, and the yellowish-green colour of the arnica tincture interfered. A second sample of somewhat deeper colour was next examined. Aniline colours were not likely to be present, therefore they had to search for vegetable colours. The tincture was rendered alkaline with ammonia and shaken out with ether, which became of a pale violet colour, which pointed to the presence of orseille. After evaporating the ether, the residue was dissolved in dilute alcohol, but the violet fluid gave, however, a total different spectrum from orseille. Dilute acetic acid turned the liquid red. Soda-ley made it blue. These liquids, the alkaline one more in particular, gave very decided spectra. Those interested in the spectroscopic investigation of similar colouring matters, we refer to the original illustrated article.

In its reaction with ammonia and ether, alkanet behaves like orseille, whilst the pigments of logwood, grape, blackberries, etc., do not colour the ether.

L. DE K.

DETERMINATION OF THE SPECIFIC GRAVITY OF HEAVY SYRUPS. AD. GENIESER (*Zeitschr. f. angew Chemie*, No. 2, 1890).—Strange as it may seem, this determination does not always give concordant results, which, the author finds, is caused by the great difficulty of freeing the syrups from air bubbles, even when they are heated a long time on the water-bath. The following process, introduced by the author, gives very concordant, almost scientifically, accurate results :—

The syrup is first passed through a sieve. A sp. gr. bottle of 50 c.c. capacity is now weighed, and after introducing about 30 c.c. of the syrup, it is reweighed after cooling. Suppose, when empty, it weighs 24.6506 grams., with syrup it weighs 79.4220; it will then contain 54.7914 syrup. The bottle is now immersed in an oil-bath or in brine, and this is heated until the syrup begins to boil, which causes all air to be expelled. After cooling to 60° F., a drop of distilled water is put on the top, which

will soon break and expel the air bubbles. The bottle is now carefully filled up with water and weighed. Suppose it weighs 89.7660 grams., then  $89.7660 - 79.4220 = 10.3240$  grams. of water have been added. The bottle holding exactly 50 grams. of water, the syrup occupied the same volume as  $50 - 10.324 = 39.676$  grams. of water. Its sp. gr. is therefore  $54.7914 : 39.676 = 1.38097$ .

L. DE K.

ESTIMATION OF CADMIUM IN ZINC REFUSE. W. MINOR (*Chemiker Zeitung* No. 1, 1890).—The author already published an accurate method in 1889, but this required a four times reprecipitation with hydrogen sulphide. This being very troublesome, the author has now devised another process. A definite quantity of the substance is dissolved in hydrochloric acid, and the cadmium separated from zinc and iron by passing a current of hydrogen sulphide. The precipitate, which always contains some co-precipitated zinc, is washed with hot water and dissolved in dilute hydrochloric acid. This solution is heated to boiling, and poured into a boiling solution of sodium hydrate. The precipitated cadmium oxide is filtered off and completely freed from zinc by washing with a 1 per cent. solution of caustic soda. The alkali is now perfectly removed by means of boiling water, and the filter is then dried. To prevent loss by reduction, the filter is ignited in a Rose's crucible, in a current of pure oxygen. The weighed cadmium oxide is then calculated to metal. If iron should be absent, the precipitation with hydrogen sulphide may be omitted, and the cadmium solution at once poured into the caustic soda.

To estimate zinc and cadmium in native zinc sulphide, the author recommends the following process. The ore is dissolved in the usual way, and then mixed with excess of ammonia which throws down the iron, and redissolves the zinc and cadmium. This ammoniacal solution is now nearly neutralised and poured into excess of boiling caustic soda, which throws down the cadmium and keeps up the zinc. The cadmium oxide is treated as described, whilst the zinc solution after neutralising the greater part of the alkali with hydrochloric acid, may be titrated with standardised sodium sulphide.

L. DE K.

FAT TITRATION. MAX GRÜGER (*Zeitschr. f. angew. Chemie*, No. 3).—In many analyses, such as the iodine absorption for fats, the estimation of carboic acid with bromine, etc., etc., it is a well-known fact that unless a large excess of the reagent has been added, the results are untrustworthy. The author now finds the same sort of thing with the Koetstorfer process for fats. No result must be trusted unless the produced soap requires at least 5 c.c. of semi-normal hydrochloric acid for neutralisation.

L. DE K.

A RAPID METHOD FOR PHOSPHORUS IN IRON AND STEEL. BY G. L. NORRIS (*Journ. Frank. Inst.*, Jan., 1890).—Five grams. of pig-iron or steel are treated in a twelve-ounce covered beaker, with 90 c.c. of 1.135 sp. gr. nitric acid for steels, 120 c.c. for pig-irons. The beaker is heated on an iron plate until all action ceases and solution begins to boil. To the boiling solution 20 c.c. of a solution of potassium permanganate, eight grams. to the liter, are added. The solution is then boiled a few minutes, to be sure all the permanganate is used up. A precipitate of manganese peroxide must come down on boiling to be sure that all the phosphorous is oxidised. After boiling with permanganate, a small piece of tartaric acid is added, and the solution boiled a minute or two longer, until all the manganese peroxide is dissolved. The solution is then poured in a 500 c.c. globe flask and 10 c.c. of 1.40

sp. gr. nitric acid added. The solution in the flask should then be about 90 c.c. in bulk. In case of pig-iron the solution is made up to 100 c.c. with water, the graphite filtered off, and 80 c.c. of the filtrate drawn off into a flask, and then 10 c.c. of 1.40 sp. gr. nitric acid added. The solution is then heated to 90° C., and 80 c.c. of ammonium molybdate solution added, the flask stoppered, wrapped in a cloth, and shaken hard for five minutes. The molybdate solution is made by dissolving 100 grams. molybdic acid in 400 c.c. strong ammonia and then mixing with 1,200 c.c. of 1.20 sp. gr. nitric acid. From this point on the method is the same as Emmerton's, reduction of the yellow precipitate with zinc and titration with a standardised permanganate of potassium solution. For high phosphorus pig-iron only 1.25 grams. are used and treated with 60 c.c. of 1.135 sp. gr. nitric acid. The solution is made up to 100 c.c., filtered, 80 c.c. of the filtrate drawn off, and 10 c.c. of 1.40 sp. gr. nitric acid added.

The only speed determination the author has made was on a steel, and thirty-six minutes covered everything, weighing and all. The test analyses are very satisfactory.

M. S. A. M.

### LAW NOTES.

#### THE LEGAL PLACE OF DELIVERY FOR COUNTRY MILK.

THIS was an appeal from the decision of the borough justices convicting Messrs. Lush, farmers, near Basingstoke, of sending adulterated milk to Mr. Lumsden, dairyman, Reading.

Mr. David (instructed by Mr. Sidney Brain) appeared for the appellants, and Mr. A. H. Spokes (instructed by Mr. F. Stevens, solicitor, Assistant Town Clerk) for the Reading Sanitary Authority.

Mr. Spokes opened the case for the Sanitary Authority. He stated that the Legislature felt that the Sale of Food and Drugs Act, 1875, was not sufficient protection to the retailer of milk in towns, who knew nothing about the milk which he received from some farmer in the country, and an Act of Parliament was therefore passed in 1879 to remedy that state of things. Any inspector of nuisances or officer having charge of the execution of the Act could procure a sample at the place of delivery and take proceedings, where the article was sold or actually delivered to the purchaser, which was in this case at Reading Station. He quoted a decision of Mr. Justice Field, that it was the intention of the Act to hit the person who sent the milk from the country. The learned counsel then stated that the contract was made in March, 1889, and the milk was delivered at Basingstoke till August 11th, when part of it was sent to Reading. On September 11th directions were given to send the whole of the milk to Reading. His learned friend was going to rely on the technical rule that the railway company were agents for the consignment. This case was exactly like the case of the delivery of milk from Coventry to Euston Station, in which nobody suggested that the delivery was at Coventry, and not at Euston Station, and the Court dealt with the case as if the milk were delivered at Euston Station.

Mr. Sinclair Campbell Lumsden, milk-seller, Minster Street, Reading, and Vine Dairy, Basingstoke, said that in March, 1889, he made a verbal contract with Mr. Thomas William Lush and Mr. Duncan Lush, farmers, Basingstoke, to deliver milk at two prices to Vine Street, Basingstoke, for twelve months. From September 11th the milk was sent to Reading Station. On September 13th witness sent a telegram to his manager to send Lush's milk that day, but no more.

Edwin Perkins, manager to Mr. Lumsden, at Basingstoke, proved that the delivery of the milk was first at Basingstoke. He sent a note by Mr. Lush's man, North, to send the milk to Reading Station. He afterwards had a conversation with one of the Messrs. Lush, and after August 11th some of the milk was sent to Reading, and the youngest Mr. Lush sometimes delivered it at the Basingstoke Station. Witness supplied the labels to put on the churns by Messrs. Lush or their men. On September 13th witness received the telegram alluded to, and sent it to Mr. Lush after their men had been to the Basingstoke railway station with the milk.

Cross-examined: The answer of Mr. Thomas Lush first was that they were willing to deliver anywhere in Basingstoke. They were willing afterwards to take the milk to Basingstoke Station to go to Reading Station. He could not refer to any specific interview after that, but he knew there were several. He never took any milk out of the churns at Basingstoke Station.

Re-examined: They never objected to take the milk to Basingstoke Station.

David North, in the employ of Messrs. Lush, said that on September 13th he took two churns from Messrs. Lush's farm to Basingstoke Station. Mr. Thomas Lush put the labels on the churns at the farm. Witness took the churns out of the cart and put them on the platform, told the porter, and he booked them. Witness saw the milk put into the train by the porter. Neither Mr. Perkins, nor Mr. Lumsden nor any of his men were at the station. Witness took the milk to the Vine Dairy and to the station at Basingstoke when it was required. Witness met Mr. Perkins about half a mile from the station, and received from him the telegram referred to.

Cross-examined: The milk was under his sole charge at the farm, and up to the time he got to

the station. He did not put anything in the milk. The churns were fastened down, but not locked. They could have been opened by anyone, but it would have taken some time in doing it.

Alfred Vicars, parcels' porter at the Basingstoke Station, corroborated the last witness, and said the churns were near the office door, and no one could have put anything into them without being seen.

Mr. W. H. Robertson, Inspector of Nuisances at Reading, proved taking a sample of milk from one of the churns when they arrived at Reading, and submitting the sample to Dr. Ashby, the public analyst.

Mr. Wright, manager of Mr. Lumsden's Reading depôt, gave corroborative evidence, and said he took the milk away from Reading Station.

Dr. Ashby proved that the milk was adulterated with not less than eighteen per cent. of added water.

Cross-examined: He took a standard which would provide against all contingencies, such as poor cattle and poor land. The milk was not like skim milk or natural milk. It was like milk with water added to it.

Mr. David submitted that the place of delivery was Basingstoke and not Reading; that the contract for delivery was at Basingstoke, and that there had never been any variation of the contract; and that the delivery took place and was completed at Basingstoke. The Inspector should have given one of the samples to Mr. Lush.

Mr. Spokes replied on the case, and submitted that a sample could not be taken at Basingstoke Station.

The Recorder said he was clearly of opinion that the conviction should be supported, because it properly came within the terms of the Act. He confirmed the conviction, and ordered the appellants to pay the costs of the appeal.

Mr. David asked for a case upon the point of delivery.

The Recorder said he would grant one if he thought there was any doubt upon the point. He had considered that point, and could not think there was a shadow of a doubt, and being of that opinion, he should stultify himself if he granted a case.

#### GUILTY KNOWLEDGE OF SKIMMING NOT NECESSARY FOR CONVICTION.

This was a case stated by the Metropolitan Police Magistrate at Dalston, and it raised the question whether it is necessary, in order to convict a vendor of milk under section 9 of the Food and Drugs Act, 1875, to show that he knew the milk had been altered.

Mr. Austin appeared for the appellant, the Inspector of Nuisances for St. Mary's, Islington, against the dismissal of the information by the Court below. On July 25th the respondent was summoned for having sold, on June 21th, 1889, an "article of food, to wit, milk, in its altered state without notice or making disclosure of the alteration, from which 28 per cent. of its original fat had been abstracted, so as to affect injuriously its quality, substance, or nature, contrary to the provision of the Sale of Food and Drugs Act, 1875, 38 and 39 Vict., c. 63, and the Sale of Food and Drugs Amending Act, 1879, 42 and 43 Vict., c. 30." It was proved that the appellant bought a pint of milk at the shop of the respondent. It was duly divided into three parts, one of which was sent to the public analyst. The certificate of the public analyst stated that 28 per cent. of fat had been abstracted, and the result of the analysis showed 1.47 per cent. of fat was all that was left. Except the certificate, no evidence was given that the milk had been altered, and the defendant gave evidence that he had no knowledge of any such alteration, and his daughter, who sold the milk and managed the shop, also denied all knowledge of any alteration. The magistrate held that, as the 9th section contemplated disclosure by the seller of the alteration of any article, it was necessary to prove knowledge of the alteration, and in the absence of such proof dismissed the summons. Mr. Austin cited the cases of "*Betts v. Armstead*" (20 Q.B.D., 771) to show that it was an offence under section 6 to sell an article not of the quality demanded by the purchaser, although the vendor did not know that it was not of the quality demanded. "*Cox v. James*" (L.R. 7, Q.B. 135) was a decision under a different Act, and was not an authority against this view. "*Cundy v. Lecocq*" (13 Q.B.D., 277) showed that a *mens rea* was not essential when the act was absolutely prohibited. "*Lane v. Collins*" (14 Q.B.D., 193) was also referred to. 38 and 39 Vict., c. 63, sec. 9, is as follows:—

"No person shall, with the intent that the same may be sold in its altered state without notice, abstract from an article of food any part of it so as to affect injuriously its quality, substance, or nature, and no person shall sell any article so altered without making disclosure of the alteration, under a penalty in each case not exceeding £20."

By section 25 it is provided:—

"If the defendant in any prosecution under this Act prove to the satisfaction of the Justices or Court that he had purchased the article in question as the same in nature, substance, and quality as that demanded of him by the prosecutor, and with a written warranty to that effect, that he had no reason to believe, at the time when he sold it, that the article was otherwise, and that he sold it in the same state as when he purchased it, he shall be discharged from the prosecution."

The respondent did not appear.

Mr. Justice Grantham regretted that no counsel had appeared on the side of the respondent, but he felt no doubt that the appeal must be allowed. In 1875 the Legislature incorporated the old Acts about adulteration of foods and drugs. The first clauses of the Act 38 and 39 Vict., c. 63, dealt with



the mixing of injurious ingredients with the articles sold. Then section 5 provided that no person should be liable to be convicted under the previous two sections if he could show that he did not know of the article having been so mixed, and that he could not with reasonable diligence have obtained that knowledge. Section 6 prohibited the sale of food and drugs not of the quality demanded. With a full knowledge of the fact that ignorance of the adulteration is stated to be a ground of exemption, section 9 was passed without any such exemption. That section dealt with two classes of persons, first with those who abstracted from an article of food, and secondly with those who sold the goods so altered. It would have been useless merely to forbid the alteration of the goods if the sale of the goods so altered were not also prohibited; for, if not, the retailer would sell it and the public would buy. The 25th section enabled a retailer to defend himself by obtaining a written warranty from the original vendor. He might hand this to the inspector of nuisances when charged with the offence. If a person did not take the trouble to get a warranty he must be held liable for breaking the law when he sold that which was expressly forbidden by the statute to be sold.

Mr. Justice Charles was of the same opinion.

#### LEGAL EFFECT OF A NOTICE OF DILUTION UNSEEN BY THE PURCHASER.

This was a case stated by justices, and raised a question under the Sale of Food and Drugs Acts. The appellant, an inspector under the above Acts, sent two of his assistants to the respondent's public-house, and they went into the club-room, owing to the bar and kitchen being full, and asked for and received half a pint of whisky. The respondent was thereupon informed that the whisky was purchased for analysis, and it was divided into three parts, in accordance with the statute. Upon analysis it was found that the whisky was diluted with water to the extent of 37½ per cent. under proof. It was proved that a notice was placed in a conspicuous place in the bar and in the kitchen that all spirits sold at that establishment were diluted with water according to price. There was no notice to this effect in the club-room. The interior of the bar was visible to a person going into the club-room. The justices found as a fact that the appellant's assistants did not see or know of any notice being posted in any part of the house. The respondent was summoned before the justices under section 6 of the Sale of Food and Drugs Act, 1875 (38 and 39 Vict., c. 63), for selling to the prejudice of the purchaser an article of food, to wit, whisky, which was not of the nature, substance, and quality of the article demanded. Section 6 of the Sale of Food and Drugs Act, 1879 (42 and 43 Vict., c. 30), allows whisky to be diluted with water to the extent of 25 per cent. under proof. The justices refused to convict, but stated a case for the opinion of the Court as to whether they ought to have convicted.

Mr. H. D. Green, Q.C., appeared for the appellant, and referred to "*Sandys v. Small*" (3 Q.B.D., 449); "*Hoyle v. Hitchman*" (4 Q.B.D., 233); "*Gage v. Elsey*" (10 Q.B.D., 518). He contended that the notice not having been brought to the knowledge of the purchasers, the sale was to their prejudice.

The respondent did not appear.

The Court remitted the case to the justices.

Mr. Justice Mathew said that it was manifest the respondent was carrying on business in the ordinary way, and had no intention of deceiving these purchasers. It was extremely curious that the purchasers did not go into the ordinary parts of the house, where they must have seen the notice. They, however, found their way into the club-room, where they were supplied with the spirits. Under these peculiar circumstances he (the learned Judge) was disposed to be extremely critical as to the findings in the case, and in his opinion it was incumbent upon the complainants to satisfy the justices that they did not know that the spirits sold in the house were diluted. There was no finding upon that point in the case. The only finding was that the complainants did not see the notice. The Court could not, therefore, satisfactorily dispose of the case without sending it back to the justices to find as a fact whether the purchasers knew that spirits sold at the respondent's house were diluted. If the justices found in the affirmative there must be no conviction; if in the negative, then the respondent should be convicted.

Lord Justice Fry said that he had doubts whether the burden of showing knowledge in the purchasers was not upon the respondent, but he was strongly inclined to think that the respondent could discharge that burden. Under the peculiar circumstances the case must go back to the justices.

#### REVIEW.

NOTES ON QUALITATIVE ANALYSIS, ARRANGED FOR THE USE OF THE STUDENTS OF THE RENSSELAER POLYTECHNIC INSTITUTE. By W. P. MASON, Professor of Analytical Chemistry. 2nd Edition. Troy, N.Y.: Nims and Knight.

THIS is a well-printed little book, possessing no very special features except that, like many works of its kind, it does not contain any attempt at an acid course worth a name. Here and there we come across a really useful note, such as one showing the student the things that must not be evaporated in a platinum dish. Over here we have many such booklets, and we do not think that there will be any room for this one in the British market. A point is made of giving always a reference to larger books for full information on matters beyond the scope of the present one, which is a commendable feature.

# THE ANALYST.

APRIL, 1890.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

AN ordinary meeting of the Society was held at Burlington House on Wednesday, the 12th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

A ballot was taken for new members, when the following were declared elected :—  
R. Hellon, Public Analyst for Cumberland; J. B. Harrison, Government Analyst, British Guiana.

Mr. H. D. Richmond, of Cairo, was proposed as a member.

The following papers were read and discussed :—

"On the Analysis of Disinfecting Powders containing Commercial Carbolic and Sulphurous Acids."—By Dr. MUTER.

"On the Chromate Test for Lead in Water."—By SIDNEY HARVEY.

"On the determination of Rosin in Soap."—By ROWLAND WILLIAMS.

The next meeting of the Society will be held at Burlington House on Wednesday, the 9th inst.

## ON THE SOLUBILITY OF PHOSPHATE OF ALUMINA IN ACETIC ACID WITH SPECIAL REFERENCE TO THE ESTIMATION OF ALUMINA IN FLOUR, BREAD, ETC.

By W. C. YOUNG, F.I.C., F.C.S.

(Read at Meeting, February, 1890.)

In previous communications to the Society I have called attention to the solubility of phosphate of alumina in acetic acid and its effect upon the "logwood" test. I propose in this paper to show to what extent this solubility affects the processes in use for the

determination of alum in bread, etc., where the phosphate of alumina is precipitated in the presence of free acetic acid, and the influence exerted by the acetate of ammonium and other compounds present in solution and by proceeding in a variety of ways.

The solutions used in the experiments to be described were of the following strengths, viz.:—Alum, 100 c.c. = 1 gram. potash alum, phosphate of sodium, 100 c.c. = 20 grams. acetate of ammonium, 100 c.c. = 20 grams. acetic acid, commercial pure.

The experiments were made in the following manner: 100 c.c. of alum solution taken in each case (the quantity of alumina present representing the amount that would be obtained from 100 grams. of bread containing about 20 grs. of alum in 4 lbs.)

No. 1. 5 c.c. acetic acid, 2 c.c. phosphate of sodium solution, and 5 c.c. acetate of ammonium solution added, boiled and then filtered.

No. 2. 5 c.c. acetic acid and 2 c.c. phosphate of sodium solution added, boiled, then 5 c.c. acetate of ammonium solution added, again boiled, and then filtered.

No. 3. 5 c.c. acetic acid, 2 c.c. phosphate of sodium solution, and 5 c.c. acetate of ammonium solution added, set aside in the cold and filtered as soon as the precipitate settled.

No. 4. 5 c.c. acetic acid, 2 c.c. phosphate of sodium solution, and 5 c.c. acetate of ammonium solution added, set aside over-night, then filtered.

No. 5. 5 c.c. acetic acid, 2 c.c. phosphate of sodium solution, and 5 c.c. acetate of ammonium solution added, boiled, and set aside over-night, then filtered.

The various solutions were added in the order given above.

In every case the liquid remained quite clear in the cold until the acetate of ammonium solution was added, when a precipitate commenced to form. In the case of experiment No. 2, a precipitate formed on boiling, which, after addition of acetate ammonium, became very dense, much more opaque and apparently larger in bulk than any of the others.

The results obtained, stated in grams., are as follows:—

|    | A.           | B.    | C.    | Mean.  |          |
|----|--------------|-------|-------|--------|----------|
| 1. | ·0230        | ·0230 | ·0210 | ·0223  | grammes. |
| 2. | ·0250        | ·0245 | ·0250 | ·0248  | „        |
| 3. | ·0218        | ·0220 | ·0205 | ·02143 | „        |
| 4. | ·0226        | ·0225 | ·0215 | ·0222  | „        |
| 5. | ·0226        | ·0225 | ·0230 | ·0227  | „        |
|    | Theory gives |       |       | ·0258. | „        |

It will be seen from these figures that in every case the result was below theory, the nearest approach being in the case of experiment No. 2.

It is curious that in No. 2 the character of the precipitate obtained differed from all the others and was larger in amount, as the only difference between it and No. 1 was that the solution was boiled after the addition of the phosphate of sodium, and again after adding the acetate of ammonium, whereas in No. 1 all the solutions were added before boiling. The lowest result obtained was in No. 3, as was to be expected.

On comparing No. 1 and No. 5 it will be seen that there is very little difference, showing that after precipitation by boiling the phosphate of alumina does not redissolve by long contact with acetic acid of the strength employed in these experiments. The increase in the precipitate by boiling is shown on comparing No. 1 with No. 3. The in-

fluence of the acetate of ammonium being so very marked I repeated experiments 1, 3, and 4, using in each case 1 c.c. of acetate of ammonium solution, or a fifth of the quantity used before, when I got the following results:—

1. .0185                      3. No precipitate.                      4. .0108 grms.

Experiment No. 2 was also repeated, using 15 c.c. of acetic acid and no acetate of ammonium, the result being .0165 gram.

No. 1 was the result obtained by filtering immediately after boiling, No. 3 in the cold, and No. 4 after boiling and setting aside over-night. No. 2 shows the degree of solubility of phosphate of alumina (precipitated from a boiling solution), with a large excess of acetic acid in the absence of acetate of ammonium. These results show very clearly that the quantity of acetate of ammonia present has a great influence on the solubility of phosphate of alumina in acetic acid.

In order to ascertain if the quantity of phosphate of alumina dissolved increased with the proportion of alum present, I repeated the five experiments, using a .2 per cent. solution of alum, with the following results:—

|    | A.    | B.           | C.    | Mean. |          |
|----|-------|--------------|-------|-------|----------|
| 1. | .0480 | .0475        | .0470 | .0475 | grammes. |
| 2. | .0505 | .0500        | .0500 | .0502 | "        |
| 3. | .0445 | .0440        | .0435 | .0440 | "        |
| 4. | .0450 | .0460        | .0460 | .0457 | "        |
| 5. | .0470 | .0460        | .0450 | .0460 | "        |
|    |       | Theory gives | .0516 |       | "        |

(On comparing these figures with the first series it will be seen that the loss in every case is slightly increased.)

The following experiments, in which 15 c.c., instead of 5 c.c., as in the former were used, show the effect of a large excess of acetic acid.

## THE ANALYSIS OF CARBOLIC AND SULPHUROUS DISINFECTING POWDERS.

By JOHN METER, PH.D., F.R.S.E.

*Read at Meeting, March, 1890.*

WHEN our Secretary pressed me to read a paper to fill up an apparent void at the February meeting, I thought that it would not be uninteresting to initiate a discussion on this subject, which is daily becoming more and more important to public analysts. Local authorities are waking up to the use of the analyst as a protector of their interests against the deceptions too often practised by unscrupulous persons, and therefore it is well that some agreement should be come to among ourselves as to the best process to employ, and also as to the best form of tender to be recommended for use by such bodies in obtaining contracts. As the latter has become really a very burning question, both to the purchasers and the trade, I propose to take it first.

The common, loose form of contract is for "carbolic acid powder containing 10 (or perhaps 15) per cent. of liquid carbolic acid at so much per ton," to which is frequently added the stipulation that "the base shall not be lime." If the words of such contract are to be interpreted in a strictly chemical sense, viz: that the powder shall contain 10 to 15 per cent. of absolute phenol, the whole thing becomes a farce; because no such

powder could be produced under a cost that would be absolutely prohibitory. All chemists know that the article commonly sold as "liquid carbolic acid" is not absolute phenol rendered liquid by the addition of 5 to 10 per cent of water, but consists of the higher phenols of coal-tar (chiefly cresol) from which the phenol itself has been nearly absolutely removed. Cresol has been held to be just as good an antiseptic as phenol, provided that it be in a free state, and especially not combined with lime. Its comparatively cheap cost, moreover, has caused it to be almost entirely employed in the manufacture of carbolic powders. Why, therefore, should this fact not be openly recognised, and all sorts of difficulties saved at once to the manufacturers, the medical officers of health, and the analyst. An analyst dealing with such a powder, and most probably employing the process originally described in the ANALYST for October, 1887, or some modification thereof, naturally reports that the powder contains so much per cent. of tar phenols (chiefly cresol); this report being laid before the authorities, some one immediately starts up and exclaims, "This is not what we want; we contracted for carbolic acid," and then the difficulty begins. An appeal is made to the medical officer, and he, answering on the spur of the moment, without an opportunity of conferring with the analyst, may simply increase the difficulty. That this is no fancy picture is evidenced by the fact that it has actually occurred in many cases, and I have at the moment in my mind an instance in which a firm, having taken such a contract, have lately been threatened that they will be compelled to supply a powder containing 10 per cent. of pure, absolute phenol, the medical officer declaring that he contracted for carbolic acid, by which he means phenol, and nothing else. In some districts the powder is also required to contain 5 per cent. of sulphurous acid without the use of the word "available," and some day we will probably meet with the *reductio ad absurdum* in the shape of a demand by a medical officer for such a powder containing 5 per cent. of free sulphurous acid—a chemical absurdity. I would therefore submit to you for consideration the advisability of impressing your Boards and the manufacturers with the necessity of ceasing to employ trade misnomers, and of contracting for a powder, the base of which shall be gypsum or siliceous matter, and which shall contain a certain percentage of uncombined tar phenols (chiefly cresol), and also, if desired, 5 per cent. of *available* sulphurous acid. I feel satisfied that in our progressive times nothing is lost, either to manufacturers or to consumers, by calling a spade a spade.

Turning now to the analytical question, I will proceed to make a few short remarks as to the basis of what will, I hope, prove to be an interesting discussion. I still estimate the phenols in carbolic powders by the process described by Mr. De Koningh and myself in the ANALYST for October, 1887, nor, despite the criticisms which subsequently appeared by Mr. Williams in the *Journal of Chemical Industry*, have I seen any necessity to alter it. The only modification I have come to in practice consists in employing 150 c.c. of 10 per cent solution of sodium hydrate instead of 200 c.c. of a 5 per cent. solution. It must also be remembered by all persons using the process that the acids, when measured over the brine, contain about 5 per cent. of water; because we have proved by experiment that commercial anhydrous cresol shaken up with brine absorbs this amount.

Speaking of commercial cresylic acid, our salt test (described in the same number of

the ANALYST) is a good and ready test to enable one to rapidly decide whether a given sample of cresol really contains water or not. Really anhydrous cresol when shaken up with three volumes of brine, gives an increase in volume of about 5 per cent. If the cresol is watery, it will either not increase in bulk at all, or it will decrease slightly. The test is of course only a safeguard against gross frauds, and for the really accurate estimation, I use the distillation process, which, when not carried too far, will enable us to read off exactly the c.c.'s of water. The amount of cresol dissolved in the water is so slight that it may be disregarded; but, on the other hand, if any appreciable amount of acid has come over, about one-tenth of its volume must be added to the water.

The ordinary cresol of commerce usually contains some naphthalene, and a rapid method of getting at a fairly accurate idea of its amount is a desideratum. This presence of naphthalene is often preferred by the purchasers who have the idea that, if "commercial carboic acid" becomes milky when put into water, it shows its strength. The process I have described is as follows:—

50 c.c. of the acid are shaken up with 200 c.c. of 10 per cent. solution of sodium hydrate, when the acids readily dissolve, leaving the naphthalene floating on the top. The bottom liquid layer is run off, a washing of 5 per cent. solution of sodium hydrate is put on, and the whole is rapidly filtered through a quick filter and allowed to drain. The collected naphthalene is then rinsed off the filter into a small beaker with water, and is then once more collected on a pair of counterbalanced filters in the usual manner. After draining, the filters are removed from the funnel and dried as far as possible between blotting paper by judicious pressure. The filters are separated, and the inner one and its contents are weighed, using the outer one as a tare. The amount of moisture held by the two filters is sufficiently alike to enable us to get a very fair approximation to the true amount of naphthalene, quite nearly enough for ordinary purposes.

Taking now the analysis of sulphurous powders, the process I use for the estimation of the available sulphurous acid is as follows:—

Two grams. of a fair sample of the powder are placed upon a small filter, and percolated with anhydrous ether until the phenols and tarry matters are removed, which is readily and quickly attained. 50 c.c. of decinormal iodine solution are then placed in a bottle, and as soon as the ether has dried off from the powder, the contents of the filter are dropped into the bottle. The bottle is allowed to stand for half-an-hour (being shaken at intervals,) and, finally, the contents of the bottle are titrated back with decinormal "hypo" in the usual manner. The amount of iodine destroyed of course represents the available sulphurous acid in the two grams. of powder started with, and, therefore, it is only needful to multiply the number of c.c. of iodine used by 0.0032. This method I find to work well with every sort of powder in the market, provided its base be not lime. To get a really satisfactory process in the presence of a lime base is very troublesome, and I cannot say that I have yet met with one that is at once rapid and good. If any member of the meeting knows one, he would be doing us all a favour to give it to us.

We come now to the important question of "reversion." Sulphurous powders oxidise with great rapidity, and a perfectly honestly-manufactured one may, if badly kept for even a very short time, show, on analysis, a much smaller portion of available

sulphurous acid than it ought to do. It is, therefore, the duty of an analyst desirous of holding the scales of justice fairly, to try, if possible, to ascertain the amount of such reversion. With a powder made on a gypsum base and with calcium bisulphite I am not aware that this is attainable; but many of the leading makers recognising this, are so constructing their powders as to render it possible. Some use a purely siliceous base, containing only a neglectable quantity of sulphate, while others use a gypsum base, but put in the sulphite in the form of a specially-manufactured sodium salt. It would, at first sight, appear that the analysis of such a powder is a very simple matter, but this is not so. The whole thing is complicated by the fact that the moment water is put upon the powder, a double decomposition occurs, and we get insoluble calcium sulphite and sodium sulphate; and we find, in practice, nearly the whole of the sulphurous acid in the insoluble residue. To get at the reversion in such powders I have devised the following method:—

20 grams. of the powder are put into a bottle, and 200 c.c. of water are measured in with a pipette. After an occasional shake, the whole is allowed to settle, and some of it is poured off or filtered through a dry filter. The decomposition above alluded to often occurs at this stage of the process; but, as will be seen, the latter is not thereby affected. 20 c.c. of the liquid (= 2 grams. of the sample), are mixed with an excess of bromine, and filtered from any bromo-cresol remaining undissolved. It is then treated with an excess of barium chloride, and the total sulphuric acid is weighed as barium sulphate. As, however, a part of this is due to dissolved calcium sulphate, another 20 c.c. are precipitated with ammonium oxalate, and the lime weighed as carbonate. The calcium thus found is now calculated to its equivalent amount of sulphuric acid, and this is deducted from the total. The remainder is still further reduced by deducting an amount of sulphuric acid equivalent to the sulphurous acid previously found by the iodine method, and the remainder represents the reverted sulphurous acid, and is calculated as such.

If the powder be made with a siliceous base, it may be more convenient for those who, only doing the analysis now and then, prefer a gravimetric method, to proceed as follows:—

Drop two grams. of the powder into a beaker containing an excess of bromine water, and while this is acting, take another 2 grams., put it into a dish, and moisten with fuming hydrochloric acid (free from chlorine). Now evaporate to dryness, redissolve, and then throw down the sulphate with barium chloride in both parts. The difference between the two results calculated to sulphurous acid will give the amount of that body present in the 2 grams. of sample taken. If the base be all but free from sulphates, we thus get a fair idea of the probable reversion at the same time.

#### DISCUSSION.

Mr. BLOUNT said that a superstitious value was generally attached to the disinfecting powers of the lower tar acids. In the specification for creosote used by the Crown Agents for the Colonies and in vogue among engineers, it was laid down that the creosote should yield not less than 10 per cent. of tar acids, of which at least half "is to be carbolic acid, distilling at a temperature not exceeding 450° F." (233° C.). Having regard to the ambiguity of the term "carbolic acid," and the risk of its being looked upon as equivalent to *phenol*, he preferred in reporting upon samples examined under

this specification to use the phrase "tar acids distilling below 450° F." as more accurate. It sometimes happened, however, that a client stickled for "carbolic acid," in which case he was accustomed to write the words in quotation marks, and indicate that the specification was responsible for them.

As to the question of extracting the tar acids, most of the creosotes he saw were of good quality, and yielded more than 10 per cent. of tar acids when the distillate below 610° F. was extracted with caustic soda, thus complying with the specification; but such samples as only just contained the permitted minimum of tar acids, and from which it was therefore important in judging them to get out every trace, were distilled to the point of pitching and then extracted.

Mr. CASSAL said that in the analysis of creosotes he had found that unless the distillation was carried to the point of pitching, the whole of the "tar acids" were not got out. He had found, further, that the passing or condemnation of a sample might depend upon the difference made by carrying the distillation to this point. Particular specifications had to be followed in which, as a rule, certain definite percentages of "crude tar acids" were mentioned. In one with which he had frequently to deal, the amount of "crude tar acids" was fixed at 8 per cent. for creosote intended for the treatment of timber, and this could certainly not be regarded as a high standard to take. Specifications for the supply of carbolic powders and liquids were, like those in use for creosote, of a very variable character. There were, in fact, all sorts of specifications and all sorts of rules laid down; it was very desirable to find out according to what authorities they had been prepared, and if possible to arrive at some sort of understanding upon the whole matter, which was at present in a state of much confusion.

He desired to mention further, firstly, that he had found it necessary in determining the tar acids to wash repeatedly with the soda solution in successive separate quantities; and secondly, after the separation of the acids to allow them to stand over the salt and acid solution for at least twelve hours. When these steps were not taken, the results were always too low, and sufficiently so to make a considerable difference.

Referring to the use of the term "Carbolic Acid," Mr. Cassal said that it could not be taken as synonymous with Absolute Phenol. The term "Carbolic Acid" had always been applied to a mixture of phenol bodies; this was the recognised trade meaning of the term, and to assert that it meant absolute phenol was to take an improper advantage of the existing confusion in chemical nomenclature. He agreed with Dr. Hunter as to the unnecessary difficulties introduced by such a proceeding. If medical men and sanitary authorities, for reasons no doubt best known to themselves, but which they would find it difficult to specify, required absolute phenol to be supplied to them, they ought to use the proper chemical term, and they would then be justified in calling upon the analyst to decide whether they had been supplied with what they had asked for.

Mr. ADAMS said that phenol was much more active as a disinfectant than as a deodorant, and there was a great difference between the two. As a true disinfectant, he thought the medical profession generally held phenol as the best of all the tar acids. Speaking for himself, he had not much confidence in any; he was quite positive that, in the ordinary way in which they were used, they exert no power as bacteriacides. He had several very interesting facts in connection with that point, and one was so clear that it was worth relating there. Many years ago he had some papers brought to his house from the secretary to his hospital. He knew that some of the secretary's children had just died of violent scarlet fever, and was consequently rather anxious about his own children; he therefore drenched the papers with a strong solution of carbolic acid, and then placed them in a window at the top of his house, exposed to the sun and out of reach, as he hoped, of his children. He was working one day at a lathe in this room,



when one of his little children got hold of some of the papers. He took her at once and washed her hands, but after three days that child had the scarlet fever. A more distinct proof of the source of infection than that could hardly be. He did not pretend that the whole of the papers were drenched through and through, but all the outside was, and they were exposed for months in the sunlight. Personally, therefore, he had very little belief in the use of carbolic acid as a bactericide; but still he did consider it was a valuable disinfectant. It had an inhibitory power over the germs, and for the time suspended their activity, but as soon as the carbolic acid had evaporated, unless it was sufficiently strong, it left the bacteria as active as ever. He could mention many other instances which had caused him to come to the conclusion that coal tar acids were useless for the positive destruction of disease germs. He had a different opinion about sulphurous acid, but the ordinary way of burning a few ounces of sulphur in a large room was not enough. A pound to a thousand cubic feet of space was required.

### ON THE CHROMATE TEST FOR LEAD IN WATER.

By SIDNEY HARVEY, F.C.S., F.I.C.

*Read at Meeting, March, 1890.*

As my paper "On the detection of lead in potable Waters by means of Potassium Bichromate," published in the ANALYST for 1881 (vol. 6, pp. 146), has apparently escaped the notice of several chemists, and as I have since had abundant opportunities of testing the extreme delicacy of the chromate reaction, I feel justified in again drawing the attention of analysts to the subject, referring for full details to my previous paper.

The  $H_2S$  test for metallic impregnation is of course a most essential one, but it is not always safe to ascribe the colour thereby struck to lead thus ignoring the possible presence of copper and tin, and it is most desirable before proceeding to quantitative results to be sure of the presence of the very metal suspected. For the purpose of proving the presence of lead nothing in my experience exceeds the delicacy of the chromate reaction, which is performed as follows:-

Half a litre of the water in question, if it can be spared (otherwise quarter of a litre will do), is placed in a conical precipitating jar (Phillips's) about two grains of  $K_2Cr_2O_7$  are added, and dissolved by agitation. The mixture is set alongside another jar containing "lead-free" water treated in a similar manner. It is assumed that the water is quite clear, if not it must be carefully filtered to render it so; the addition of any acid is objectionable, and previous concentration is unnecessary and even injurious. The use of the bichromate in *crystals* is also essential.

Water containing as little as one fiftieth of a grain per gallon of lead will, when thus treated, become sensibly turbid in about fifteen minutes, and the turbidity is rendered the more apparent by contrast with the jar alongside. In about twelve hours, if undisturbed, the precipitate will have completely settled, and the fluid may be poured off to the *last drop*, leaving the bottom of the jar coated with the  $PbCrO_4$ , which latter may be rendered much more distinct by mixing it with a few c.c.'s of distilled water, and allowing the same once more to settle in a narrow flat bottom tube. Of course, in the case of waters containing larger amounts of lead than the above, the reaction is much more prompt and decisive.

No other metal likely to be present in water will give a similar reaction, and I am inclined to think that this test for lead is amply sufficient for all practical purposes. One fiftieth of a grain per gallon of lead is equivalent to one part in three and a half millions or to one part of  $PbCrO_4$  in two and a quarter millions, thus demonstrating the remarkable insolubility of chromate of lead.

*(Conclusion of the Society's Proceedings.)*

## DETECTION AND QUANTITATIVE ESTIMATION OF INORGANIC AND ORGANIC POISONS IN BODIES.

BY DR. ANTON SEYDA.\*

## INTRODUCTION.

ALTHOUGH toxicologists have at their disposal a vast amount of chemical literature, I hope this article will be welcome to many, particularly as it is the result of my own experience and observations. My object has been to find a practical qualitative and quantitative course for the detection of those poisons which are within reach of the public, without troubling about such bodies as bitters, drastics, etc., which, in the present state of science, cannot be detected with certainty, whatever care and material the analyst might waste on the matter.

The analysis consists of a preliminary examination, and the regular chemical course. The expert conducting such an investigation must never omit to make the fullest inquiries about the case, as often valuable clues will be obtained, saving an immense deal of time and trouble.

## PRELIMINARY TESTS.

*(a) Blood.*

The blood is often in a state of partial decomposition, particularly if a long time has elapsed between the time of death and the investigation. The reduction of its colouring-matter is more or less complete, so that a spectroscopical examination is, of course, useless. If the blood should be dry, it may be dissolved by water containing a trace of caustic soda. The spectrum of a partially reduced blood mostly shows a continued broad absorption band, which is composed of three lines, viz., two of oxyhæmoglobin, with the hæmoglobin one between. Sometimes the band is accompanied by another line in the red part of the spectrum, which is due to either hæmatin or methæmoglobin.

If this fourth line is observed, the blood must be tested as to its reaction. If alkaline, this points to methæmoglobin; if acid, to hæmatin. The first case deserves but little attention, as a rule, unless there has been poisoning with hydrogen sulphide (which is not likely to originate from the putrefaction process), but the second points to the administration of acids, nitroglycerin, potassium chlorate, or ferrocyanide or nitrobenzol. These bodies will then have to be searched for in the urine and other parts of the body.

In most cases, the only question is to decide whether the blood contains carbonic oxide. If we have to deal with a blood whose oxyhæmoglobin has been completely converted into the carbonyl compound, without the reverting process having set in, the detection of the carbonic oxide is easy, chemically as well as spectroscopically. If the blood, however, only shows the lines of the non-reduced or partially reduced hæmatin, the detection of the carbonic oxide is not successful, and, in fact, not likely to be so.

Not unfrequently, a blood will have to be examined for carbonic oxide, when it contains carbonylhæmoglobin, oxyhæmoglobin and hæmoglobin, with perhaps methæmoglobin or hæmatin.

In such a case, the presence of the carbonyl compound can only be proved by

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\* *Chemiker Zeitung*, slightly abridged.

adding ammonium sulphide, and noticing whether the absorption band moves towards the red part of the spectrum. The chemical testing with soda ley, with or without calcium chloride, is not trustworthy.

(b) *Urine.*

In testing this, it must be noticed this fluid undergoes remarkable changes whilst the poison is acting; also that many poisons only then pass into it when their physiological action is over. Therefore ascertain, if possible, the quantity of the urine, then look at its colour, notice the smell, test for blood, albumen, sugar, also its behaviour towards barium chloride, both before and after addition of hydrochloric acid.

The urine may also contain volatile bodies, balsams, alkaloids, and poisonous metals; whilst if poisonous doses of potassium chlorate, iodide or bromide have been given they will be readily detected in this fluid.

(c) *The contents of the Stomach.*

After noticing the odour and reaction, try whether there is a phosphorescence in the dark. If the stomach has an alkaline reaction, any phosphorescence cannot be due to phosphorus, but is caused by a fungoid growth, then phosphorus only lights when the contents are acid. The reaction of the contents will, according to circumstances, be acid, alkaline, or neutral. Poisoning caused by corrosive acids, caustic alkalies, or haloids, is sure to have been recognised by the medical man who conducted the post-mortem examination.

The odour will not give much information if the contents are much putrefied. But when they are apparently in a good state of preservation, I have often noticed a loathsome, sweetish smell in the case of a decided form of arsenical poisoning. If the contents are solid, it is best to take an aliquot part and digest it in a small beaker with spirits of wine, and finally wash the insoluble matter with ether. The residue must now be rigorously examined with the microscope, which will often show remnants of medicines, pills, or powders. The alcoholic solution may be tested for oxalic acid. In many cases the stomach has been washed out for the purpose of the post-mortem. In this case the sediment of the wash-water must be carefully examined. Many indifferent objects will often be found, such as particles of carbon, fragments of coffee, potatoes, grain, greens or flesh, also crystalline bodies, such as triple phosphate, if the stomach has an alkaline reaction. If seeds are found they must be well washed with water, alcohol and ether, sorted, weighed and examined. If particles of arsenious acid are noticed, they may, after being freed from adhering matter, be gently dried and weighed, or dissolved in solution of potassium bicarbonate, and titrated with iodine. When the microscopical investigation is over, it is, in many cases, advisable to take a little of the contents and test for arsenic first, as this is the commonest form of poison. If not found, another portion may be exhausted with water, and the filtrate be examined for soluble metallic salts, more particularly the chlorate, nitrate, iodide, bromide, ferro or ferricyanide of potassium.

2.—SPECIAL PART.

If the preliminary testing has given no particular indication, I start the chemical analysis. I first of all submit the organs to a fractional distillation. The residue

left in retort is then exhausted with alcohol to dissolve out any alkaloids, and then afterwards chlorinised for the purpose of testing for metallic poisons.

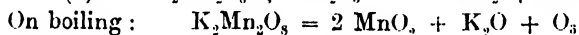
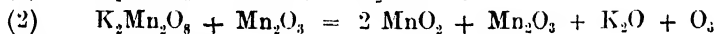
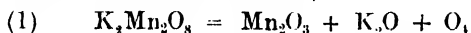
#### VOLATILE BODIES.

The contents of each jar are examined separately. A portion is cut up into small pieces and put into a suitable retort containing water. The first distillation is done by immersing the retort in boiling water for several hours. I then add to the contents a little tartaric acid and once more distil, this time by means of a current of steam. In this way we get two fractions. The first contains the readily volatile bodies, such as alcohol, aldehyde, acetone, chloroform, nitrobenzol, turpentine, camphor, amines, or their sulpho-derivatives. In the second, the remnants of the first, further fatty acids, carboic acid, hydrocyanic acid, phosphorus, etc. If chloral hydrate or potassium cyanide\* are suspected, the organs are moistened with respectively caustic potash or sodium bicarbonate and distilled from the water-bath, but should it be necessary to conduct a steam distillation from an alkaline fluid, I prefer to first make an acid extract with water containing some tartaric acid, which is then filtered and made alkaline before distilling.

If the acid distillate is ready, I properly notice its reaction, colour, odour, degree of turbidity, and particularly its bulk, so as to be able to make a quantitative estimation of any substance (such as alcohol) which the distillate may contain.

#### THE FIRST FRACTION.

(a) Test with acid silver nitrate; (b) with ammoniacal ditto (aldehyde); (c) with nitroprusside, potash, and acetic acid (aldehyde, acetone). Then test with alkaline permanganate (d) as follows:—10 c.c. of distillate are mixed with a few drops of potash ley and 1 c.c. of a saturated solution of permanganate and allowed to stand for twelve hours in a closed vessel. If oxidisable bodies are present, reduction soon sets in and the permanganate gets decolorised. The filtrate is then tested for aldehyde with ammoniacal silver. A large increase in the amount of aldehyde points to the presence of alcohol. As is well known, an alkaline permanganate acts differently in the cold than at the boiling heat. In the cold the following reaction takes place (in presence of organic matter):—



It is highly probable, although not yet proved, that in the cold the liberated oxygen will first act on any organic matter before peroxidising the manganic oxide.

(e) With iodine and potash ley as follows:—In a test-tube I introduce a pinch of iodine, then 10 c.c. of the fluid and 3 drops of a 30 per cent. potash, then heat to 50° C., when, owing to the formation of iodoform, the liquid will get more or less turbid. If the iodine is used up, a little more of it must be added, and its excess finally be removed by cautious addition of potash ley. As iodoform does not always separate in well-defined crystals, the best thing is to agitate the solution with

\* Supposing there is also a ferrocyanide.

## THE ANALYST.

ether and allowing the latter to evaporate. If after a microscopical examination of the residue there is still a doubt, Lustgarten recommends the treatment of the crystals with resorcin and potash to get rosolic acid. (*f'*) With resorcin and potash (chloroform). I have slightly modified Lustgarten's test. In a tube introduce a pinch of resorcin, 10 c.c. of the distillate, 3 drops of a 30 per cent. potash ley, and warm gently, when the beautiful rosolic acid is soon formed. This test is more delicate than the isonitril test; then however powerful and characteristic the smell may be, it is often masked by the presence of amines. In regard to the prussian blue test (treatment of chloroform with alcoholic ammonia and potash), although when performed under pressure a good result may be obtained, this test is far inferior to the rosolic acid test. (*g*) Zinc dust and hydrochloric acid (nitro-benzol). 10 c.c. of distillate are mixed with an equal volume of 90 per cent. alcohol, a little zinc dust is added, then 1 c.c. of hydrochloric acid, and a drop of platinic chloride. After standing for three hours, the liquid is decanted from the undissolved zinc and the greater part of the spirit driven off on the water-bath. The residue is now diluted with water, rendered alkaline with potash, and shaken out with ether. The ether is evaporated and the residue tested for aniline with freshly prepared solution of chloride of lime, which will produce a blue colour should nitro-benzol have been present. (*h*) With hydrochloric acid and alcoholic solution of phloroglucin (etheral oils). This test, proposed by Ihl for the detection of bodies of an aldehydic nature, will often give unreliable results when applied to the distillate of portions of bodies, but it is best applied to the distillate of the urine. Hager's test for oil of turpentine is best carried out as follows:—A pinch of guaiacum is dissolved in 1 c.c. of absolute alcohol and 5 drops of oil of lemon and the mixture boiled; 10 c.c. of distillate are added and the whole boiled once more. The test only succeeds when notable quantities of turpentine are present and the reagent must be quite fresh. If, however, the distillate should have no action on alkaline permanganate or solution of chromic acid, ethereal oils are out of the question.

A quantitative estimation of these volatile bodies will not often be practicable, not so much because no proper processes exist, but chiefly on account of the scarcity of material. An exception, however, is the estimation of the alcohol. Any one who has often had occasion to quantitatively determine alcohol in poisoning cases will often wonder how it is so comparative little attention has been paid to this subject in the works on toxicology and even chemistry. Rarely will the contents of the stomach be in such a fresh condition and the amount of alcohol so large as to admit of the estimation of the alcohol by the usual process, viz., distillation and specific gravity, more particularly as the gravity may be altered by the presence of amines. Even addition of mineral acids or even platinic chloride and redistilling will not altogether remove the organic bases. The only way is to oxidise the alcohol to acetic acid and to estimate this volumetrically. I carry out this estimation as follows:—The distillate is once more distilled off. What passes over in the first quarter of an hour is collected into a receiver containing some dry potassium carbonate. The process is repeated until we finally have a distillate measuring about 10–20 c.c., mostly strongly ammoniacal. It is put into a high-pressure flask, mixed with 3 c.c. of a twenty per cent.

solution of potassium bichromate, and, after being placed in a freezing mixture, mixed with about 10 c.c. of strong sulphuric acid, or more if the iodoform test has been very successful. After closing the flask it is heated in boiling water for eight hours. After cooling, the contents are put into a flask (kept cool), supersaturated with potash, and boiled until every trace of compound ammonias has completely disappeared, which is readily ascertained by exposing to the vapours a piece of red litmus paper.

After acidifying the solution with sulphuric or phosphoric acid, it is distilled (by means of introducing steam) until the distillate is no longer acid. The distillate, often measuring a litre, is titrated with  $\frac{n}{10}$  soda, using *litmus* as indicator. The alcohol is then calculated from the amount of acid found, and it must then be re-calculated to the original volume of the distillate. To make sure the distillate really contained acetic acid, the neutralised fluid is boiled down to a small bulk. An aliquot part is tested with barium chloride, and should there be any precipitate, it must be collected and allowed for. Another portion is mixed with a few drops of alcohol and then with sulphuric acid in excess. If after twenty-four hours there is a strong odour of acetic ether, the presence of acetic acid, therefore the presence of alcohol is proved beyond doubt. Or we may apply Carstanger's well-known caccodyl test.

The principles of the method just described will be easily understood. I must, however, point out the absolute necessity of thoroughly boiling the oxidised mixture with potash, otherwise the process is bound to fail. The amines always pass into the alcoholic distillate, even if distilled from an acid solution. They are not acted upon by the oxidising mixture, and, therefore, unless removed by boiling with caustic potash, they would again get into the acetic distillate.

As already stated, not much importance seems to be attached to the qualitative and quantitative toxicological determination of alcohol; not so much because there were no reliable processes, but principally because it is only reckoned a poison in its pure state. I hold, however, a quite different opinion. Think how alcohol in its various forms, from brandy to methylated spirits, is within almost everybody's reach, and how easily it may be abused; not so much in the case of grown-up people, but helpless infants. Is it not a well-known fact, that gin, for instance, is largely administered to infants to make them sleep, and how many have not in this way been killed by their unnatural mothers, without these in the least being suspected? Are not two tablespoonfuls of corn brandy often a *fatal* dose for a child of six months old? Is it not probable that among the lower classes this comparative safe way of infant poisoning is largely practised? The chemical detection of alcohol is beset with difficulties; then first of all it rapidly passes out of the system, and it has also been proved that traces are actually formed in the living organism, whilst it is even a product of putrefaction. I therefore must insist upon the quantitative estimation of the spirit, which, if the amount should be excessive, will point to the use of alcoholic liquors, or even tinctures, or may be in other respects a valuable clue.

(To be continued.)

## ON A VOLUMETRIC METHOD OF GENERAL APPLICABILITY FOR THE DETERMINATION OF COMBINED SULPHURIC ACID.\*

BY LAUNCELOT W. ANDREWS.

Of the volumetric methods at present in use for the determination of sulphuric acid, none can be considered entirely satisfactory, although some of them are very useful for technical purposes. Several of these methods involve a double titration, some require three standard solutions, and others are only applicable in the absence of bases precipitable by sodium carbonate.

The author believes, therefore, that the presentation of a new method, applicable in the presence of magnesium, calcium, aluminum, zinc, manganese, iron (ferrie), nickel, cobalt, and silver, which requires but one standard solution with a single titration, and which in precision is at least equal to the ordinary gravimetric determination as barium sulphate, while demanding much less time for its execution, will not be thought superfluous.

The process depends upon the following series of reactions: First, to the solution of a sulphate is added an excess of a solution of barium chromate in hydrochloric acid; second, the solution is neutralised with ammonia or calcium carbonate, and filtered; third, the filtrate is acidified with hydrochloric acid, potassium iodide added, and the free iodine titrated with decinormal sodium thiosulphate solution (1 c.c. = 12.654 mg. iodine = 2.662 mg.  $\text{SO}_2$ ).

The barium chromate employed may contain barium sulphate, but must be completely freed from soluble chromates and from barium carbonate, nitrate or chloride, by prolonged washing, first with boiling water slightly acidified with acetic acid, finally with hot distilled water, until the washings give no precipitate with sulphuric acid, and (in a quantity of 100 c.c.) a barely perceptible reaction with hydrochloric acid, potassium iodide and starch paste.†

A suitable solution of the barium chromate is prepared by digesting it with hydrochloric acid containing 36 grms. acid in the litre. This solution will contain from 2 to 4 per cent. of barium chromate, according to the temperature at which it was prepared.

The reagent being ready, the analysis is performed as follows:—

The sulphate to be determined is diluted, if necessary, until it does not contain more than 2 per cent., at most, of sulphuric anhydride, is made approximately neutral, and is heated to boiling. While boiling hot, an excess of the barium chromate solution is gradually introduced, and the boiling continued one minute, or longer, if carbonates were present.

The precipitate of barium sulphate is always yellow from the barium chromate which is carried down with it, provided sufficient excess of the latter reagent was added.

\* *American Chemical Journal*.

† When barium chloride is precipitated with an excess of potassium chromate, the water with which the precipitate is washed will, for a long time, show a yellow colour. This is not, as has been supposed, due to the solubility of  $\text{BaCrO}_4$ , but to the fact that it obstinately retains soluble chromate. According to the author's observation, barium chromate is not sufficiently soluble in water to impart any colour to the latter. According to the mean of four concordant determinations, one million parts of water dissolve 15 parts barium chromate at  $18^\circ\text{C}$ .

Calcium carbonate, which must be entirely free from barium or strontium carbonates or calcium sulphate, is then thrown in small portions into the still hot liquid until no further evolution of carbonic anhydride is observed, and the boiling continued one or two minutes. The solution is filtered while hot, and the precipitate is washed with a small quantity of hot water until the washings are colourless, and a little longer. Under these conditions, the barium chromate has no tendency to run through the filter or to retain any soluble chromate. 75 c.c. of water will usually be found more than sufficient to effect the washing.

If, on the other hand, the solution is allowed to stand over night with the precipitate in it, calcium chromate will be retained and a longer washing becomes necessary. In this case the results may come somewhat too high, in consequence of the necessarily large amount of wash-water dissolving an appreciable quantity of barium chromate. Under normal conditions the error from this source is quite insignificant.

The filtrate, after cooling, is treated with a sufficient amount of crystals of potassium iodide (free from iodate) and with 5 to 7 c.c. fuming hydrochloric acid for each 100 c.c. of liquid. This amount of acid is enough to induce a prompt and complete reduction of the chromate, but not enough to decompose the starch paste. It is advisable to run in the decinormal sodium thiosulphate from a burette until the brown colour of the iodine is nearly discharged before adding the starch, and then to continue the titration slowly, with constant stirring, until the turning point is reached.

The above process must be modified in the presence of ferric, nickel, or zinc salts by using ammonia instead of calcium carbonate to neutralise the acid liquid. The solution in this case is to be made distinctly alkaline, and the excess of ammonia boiled nearly away before filtering. The necessity for this modification arises from the fact that if a ferric or nickel or zinc salt is boiled with a chromate and calcium carbonate, basic chromates of iron and nickel are precipitated, from which the chromic acid cannot be removed, or only with difficulty, by washing. Barium chromate, when precipitated from its acid solution by ammonia, does not possess the agreeable properties which it shows when thrown down by calcium carbonate. It is much more finely divided than in the latter case, tends to run through the filter, which must therefore be double or of very dense paper, and requires a longer washing to remove the soluble chromates which it more tenaciously retains; consequently, ammonia is only to be used when the employment of calcium carbonate is inadmissible. It is not practicable to precipitate the excess of barium chromate with sodium acetate from hydrochloric acid solution. Numerous experiments, the details of which it is not worth while to give, show that barium chromate is so soluble in hot dilute acetic acid that the results fall 3 to 5 per cent too high, while if precipitated cold and allowed to stand, the results are too low.\*

The following analyses show the applicability of the method :—

I. Taken 10 c.c. of a solution containing 20·8984 grams. pure and dry ammonium sulphate per litre. Diluted to 50 c.c., treated with 15 c.c.  $\text{BaCrO}_4$  solution with  $\text{CaCO}_3$ , as described above.

\*The method cannot be used in the presence of phosphoric acid, and, of course, all reducing agents, as well as bismuth and copper salts, must be excluded.



Required 47.60 c.c.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol. = .1267 gram.  $\text{SO}_3$  found. Calculated, .1266 gram.  $\text{SO}_3$ ; 100.08 per cent. found.

II. Taken 10 c.c. of the same ammonium sulphate solution and treated as in No. I. Required 47.60 c.c.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol.

The volume of the solution before titration was 300 c.c. 100.08 per cent. found.

III. 20 c.c. of the same ammonium sulphate solution, treated as before, required 95.50 c.c.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol.

Total volume of the solution, 400 c.c.; 100.37 per cent. found.

IV. Taken .2980 gram.  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ , small crystals obtained by triple recrystallisation of a commercial sample. The copper was precipitated from boiling sol. with  $(\text{NH}_4)_2\text{S}$  (free from sulphate), solution boiled with acetic acid to expel  $\text{H}_2\text{S}$ , filtered and filtrate treated as above.

35.95 c.c.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol. required = .0957 gram.  $\text{SO}_3$  = 32.11 per cent. found. Theoretical per cent. = 32.09.

V. Taken 10 c.c.  $(\text{NH}_4)_2\text{SO}_4$  solution (see 1) containing .20898 gram., diluted to 100 c.c., treated with 20 c.c.  $\text{BaCrO}_4$  sol. as above and neutralised with ammonia. Required 47.30 cc.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol. = .1260 gram.  $\text{SO}_3$  instead of .1266 gram. Found 99.52 per cent.

VI. Taken .6485 gram.  $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ . Treated as No. V. Required 80.65 c.c.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol. = .2147 gram.  $\text{SO}_3$ . Calculated .2153 gram.  $\text{SO}_3$ . Found 33.11 per cent.  $\text{SO}_3$ . Theory 33.20 per cent.

VII. a. Taken 100 c.c. of the Iowa City watersupply. Treated as No. V. Required 2.10 c.c.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol.

b. Taken 200 c.c. ditto, ditto. Required 4.30 cc.  $\frac{1}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  sol.

Found 56 mg. and 57 mg.  $\text{SO}_3$  per litre. A gravimetric analysis gave 58 mg.  $\text{SO}_3$  per litre.

It seems probable that an indirect determination of sodium and potassium would be possible by weighing these elements as sulphates and determining the sulphuric anhydride volumetrically as described. Experiments to test this are now in progress. If feasible, it is evident that it would often be more convenient than the usual indirect determination as chlorides, while free from some of the well-known sources of error involved in the gravimetric determination of sulphuric acid in the presence of alkalis.

It is both a duty and a pleasure for me to take this opportunity to express publicly my thanks to Mr. F. W. Spanutius, instructor in chemistry here, for the zeal and skill with which he has assisted me in the experimental part of this investigation. Some of the test analyses given above were performed by him.

## ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

(Read at the December Meeting of the Chemical Section of the Franklin Institute.)

THE study of the electrolysis of the double cyanides of cadmium, copper and zinc, enabled us to formulate conditions, by which the separations of cadmium from zinc (*American Chemical Journal*, 11, 352) and cadmium from copper (*Journal of Analytical Chemistry*, 3, 385) were possible, and in every particular satisfactory.

The ease with which cadmium was separated from zinc, and the very close results obtained with these metals, led us to apply the method to the separation of cadmium from cobalt and from nickel. Operating first with cadmium alone, we dissolved sufficient pure sulphate in water, so that 10 c.c. of the solution would contain 0.1688 grams. metallic cadmium. To this volume (10 c.c.) were added four and one-half grams. pure potassium cyanide, and the solution made up to 200 c.c. with water. A current yielding 0.4 c.c. O-H gas per minute was allowed to act upon the same for a period of fourteen hours. The deposited metal weighed 0.1686 gram., a difference of -0.11 per cent. from the theoretical. A second trial, with conditions precisely analogous to those just mentioned, gave 0.1690 gram. cadmium, a difference of +0.11 per cent. from the theoretical.

## CADMIUM FROM COBALT.

In the third experiment the conditions were the same as before, with this difference, that an equal amount of cobalt was also present in the solution. The result of the electrolysis was 0.1689 gram. cadmium, a difference of +0.05 per cent. from the required.

The fourth experiment, similar in every way to the third, yielded 0.1689 gram. cadmium, a difference of +0.05 per cent. from the theoretical.

The cadmium was fully deposited on both occasions, and contained no cobalt.

## CADMIUM FROM NICKEL.

Passing to the separation of cadmium from nickel, the results were so surprising that we give the same in detail, although negative in character.

|    | Cadmium present, in grams. | Nickel present. | Potassium Cyanide, in grams. | Total Dilution. | Strength of current in c.c. O-H gas per minute. | Cadmium found. |
|----|----------------------------|-----------------|------------------------------|-----------------|---|----------------|
| 1  | 0.1688                     | 100 per ct.     | 4½                           | 200 c.c.        | 0.3 c.c.  | 0.1717         |
| 2  | "                          | "               | "                            | "               | "   | 0.1702         |
| 3  | "                          | "               | "                            | "               | "   | 0.1725         |
| 4  | "                          | "               | "                            | "               | "   | 0.1750         |
| 5  | "                          | "               | "                            | "               | "   | 0.1721         |
| 6  | "                          | "               | "                            | "               | "   | 0.1737         |
| 7  | 0.1828                     | —               | "                            | "               | 0.5 c.c.  | 0.1827         |
| 8  | "                          | 75 per ct.      | "                            | "               | "   | 0.1923         |
| 9  | "                          | 50 per ct.      | "                            | "               | 0.15 c.c.                                       | 0.1841         |
| 10 | "                          | "               | "                            | "               | 0.5 c.c.  | 0.1882         |
| 11 | "                          | 25 per ct.      | "                            | "               | 0.15 c.c.                                       | 0.1854         |

The period of time during which the current acted in each of the above experiments was sixteen hours. Nickel was always found in the cadmium deposit, while in many cases the precipitation of the cadmium was incomplete. The conditions were varied, yet the results were wholly unsatisfactory. By greatly increasing the quantity of cyanide, we discovered that the cadmium precipitation was retarded. Nickel when alone, and when under the conditions given above, would not deposit with the strength of current used by us. This behaviour is only another indication that if we would

make electrolytic methods widely applicable, it is first necessary to extend the study of the action of the current to all the salts possible, and to investigate carefully the influence of each metal upon its associates under varying conditions.

From what we have thus far accomplished, we find the electrolytic separation of cadmium from copper, from zinc, and from cobalt, in cyanide solution, all that could be expected from any method. The cadmium deposits, in the experiments recorded in this paper, were always washed with boiling water; the drying was done upon the edge of a warm iron plate.

We have already called attention (*American Chemical Journal*, 11, 264) to the fact that mercury is fully precipitated from the solution of its double cyanide by a comparatively feeble current, and that the separation of this metal from copper is possible so long as the quantity of the latter does not exceed twenty per cent. of the mercury present.

More recently we have executed a series of experiments looking to the separation of mercury from zinc, nickel, and cobalt.

#### MERCURY FROM ZINC.

The results with these metals are:—

|   | Mercury present in grams. | Zinc present. | KCN in grams. | Total dilution. | Current strength in c.c. O. <sub>2</sub> gas per minute. | Mercury found. | Difference in per cent. from the theoretical. |
|---|---------------------------|---------------|---------------|-----------------|--|----------------|---|
| 1 | 0.1715                    | —             | 4½            | 200 c.c.        | 0.3 c.c.   | 0.1717         | + 0.12 per cent.                              |
| 2 | “                         | —             | “             | “               | “  | 0.1715         | “   |
| 3 | “                         | 100 per ct.   | “             | “               | 0.25 c.c.  | 0.1706         | - 0.52 per cent.                              |
| 4 | “                         | “             | “             | “               | “  | 0.1709         | 0.34 per cent.                                |

The time in each deposition was sixteen hours. From these figures the separation is possible. Mercury was not found with the zinc. In the following experiments it will be observed that the error is much less, and accordingly makes the method trustworthy and, from its accuracy, well suited for scientific as well as technical work:—

|    | Mercury present in grams. | Zinc present. | KCN in grams. | Total dilution. | Current strength in c.c. O. <sub>2</sub> gas per minute. | Mercury found. | Difference in per cent. from the theoretical. |
|----|---------------------------|---------------|---------------|-----------------|--|----------------|---|
| 5  | 0.2440                    | 100 per ct.   | 3             | 200 c.c.        | 0.5 c.c.   | 0.2435         | - 0.20 per cent.                              |
| 6  | “                         | “             | 3             | “               | “  | 0.2445         | + 0.20 “                                      |
| 7  | “                         | “             | 4½            | “               | “  | 0.2441         | + 0.04 “                                      |
| 8  | “                         | “             | “             | “               | 0.28 c.c.  | 0.2445         | + 0.20 “                                      |
| 9  | “                         | “             | “             | “               | “  | 0.2431         | + 0.37 “                                      |
| 10 | “                         | “             | “             | “               | “  | 0.2454         | + 0.50 “                                      |

The time of precipitation, made at the ordinary temperature, amounted to sixteen hours. The mercury deposit was washed with hot water, and dried upon a moderately warm iron plate.  
(To be continued.)

## REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

**ESTIMATION OF URIC ACID BY SODIUM HYPOBROMITE.** M. BAYRAC (*Compt. rend.*, 17 Feb., 1890).—50 c.c. of the urine are evaporated on the water-bath. The residue is treated with 5 to 10 c.c. of diluted hydrochloric acid (1 in 5), and the precipitate is washed with alcohol to remove urea and creatinine. It is then dissolved on the water-bath with 20 drops of solution of sodium hydrate and heated to nearly boiling with 15 c.c. of saturated solution of sodium hypobromite in the usual apparatus for urea estimations. The whole process can be performed under two hours. M. S. A. M.

**THE FERRIC CHLORIDE TEST FOR COCAINE.** PROF. PLUGGE (*Ned. Tydschr. v. Pharmacie, etc.*, March, 1890).—Messrs. Lerch and Schärge have lately published a delicate test for this alkaloid. A drop of very weak ferric chloride is added, and the mixture heated to boiling. A blood-red colour is developed, almost resembling ferric sulphocyanide. And apparently nothing is more natural. Does not cocaine on boiling with water decompose into ecgonine, methylic alcohol, and benzoic acid? And does not this acid give a red (?) colour with ferric chloride. How scientific this may all seem, the author found, however, that the same colour may be just as readily got by applying the test *without cocaine*, for reasons which any one acquainted with the chemistry of iron salts will readily understand. L. DE K.

**NEW TEST FOR CONINE.** VAN SENUS (*Ned. Tydschr. v. Pharmacie, etc.*, March, 1890).—This alkaloid gives a fine blue, changing to red and yellow when mixed with nitro-benzol. Aniline and nicotine do not give the reaction. The test is, however, not successful with the pure  $C_8H_7NO_2$ , but only with the article prepared by acting with nitric acid on *commercial* benzol. When such nitro-benzol is distilled, the first fractions give the reactions but very imperfectly, but the residue left in the retort produces a fine display of colours. The author soon hopes to be able to find out to what substance the reaction is really due. Not unlikely it may be caused by the presence of carbonic sulphide in the crude benzol. L. DE K.

**ADULTERATION OF LINSEED OIL.** PROF. WEFERS BETTINK (*Ned. Tydschr. v. Pharmacie, etc.*, March, 1890).—A sample submitted to the author, although conforming to the standards of purity as at present laid down, was, however, perfectly useless for painting purposes, as when mixed with white lead this became brittle in a few hours. This pointed to a large amount of free acid, which induced the author to apply the process of Salskowski, viz., dissolving in ether-alcohol and titrating with  $\frac{n}{10}$  alcoholic potash. Thirty-four per cent. of free (oleic) acid was thus found. To ascertain the nature of the acid, a large quantity of the oil was agitated with a 10 per cent. solution of common soda. After the greater part of the oil had separated it was agitated with petroleum spirit to free it from oily matter, and then decomposed with acid. The fatty acids thus separated gave a I. absorption of 146. (No doubt this figure would have been higher still if any stearic acid had been first removed.) The author hesitates to call it linoleic acid, but feels pretty sure it has been wilfully added. L. DE K.

**ESTIMATION OF FREE ACID IN SOLUTIONS OF STANNOUS CHLORIDE.** W. MINOR (*Zeitschr. f. angew. Chemie*, No. 1).—The estimation of hydrochloric acid in solutions of stannous chloride cannot be done with silver nitrate, as insoluble stannic hydrate would be formed as well as silver chloride. The author recommends the following process:—

10 c.c. of the fluid are diluted with hot water, and hydrogen sulphide is passed until all the tin is precipitated. The liquid is filtered off from the precipitated stannous sulphide in a litre flask. After making up the contents to the mark, 500 c.c. (= 5 c.c. original fluid) are boiled for a short time to expel the hydrogen sulphide, and finally titrated with normal soda. This will give both free and combined hydrochloric acid.

The amount of combined acid may of course be readily calculated from the amount of stannous tin, which the author prefers to estimate with iodine. If the sp. gr. of the fluid is known, the amount of acid by weight can be readily calculated.

L. DE K.

**ARTIFICIAL COFFEE IN GERMANY.** R. WOLFFENSTEIN (*Zeitschr. f. angew. Chemie*, No. 3, 1890).—The author analysed two varieties, known in Germany as Domkaffee and Allerweltskaffee. The complete absence of caffeine undoubtedly proved the absence of coffee. The microscope showed the first article to practically consist of chicory, whilst the other one contained large quantities of lupines. The author also succeeded in isolating a brown colouring matter, possessed of the same properties as the well-known Casseler-brown. It not only behaved spectroscopically the same, but also in its chemical reactions. Although soluble in alkalis and in water, it is completely precipitated by addition of mineral acids, such as hydrochloric acid. 14 grms. of the sample were extracted with water and precipitated with hydrochloric acid, which yielded 1.67 gm. of colouring matter, which corresponds with 11.9 per cent. adulteration.

## REVIEWS.

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# THE ANALYST.

MAY, 1890.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

### ON THE DETERMINATION OF RESIN IN SOAP.

BY ROWLAND WILLIAMS F.I.C., F.C.S.

*Read at Meeting, March, 1890.*

SEVERAL chemists have devised methods of greater or less value for the purpose of estimating resin in soap and in fatty substances generally, but few of these can be regarded as really satisfactory. Among the processes in vogue at different times may be mentioned those of Barfoed and Sutherland. The former of these depends upon the alleged practical insolubility of dry soda soaps (made from ordinary fatty substances) in a mixture containing five parts ether and one part alcohol, while resinate of soda is said to dissolve easily in this solvent.

Sutherland's method consists in oxidation of the resin by means of nitric acid, which is assumed to remove resin without attacking fatty acids. I have not found either of the above methods at all reliable, more especially the latter. Indeed, until a few years ago, it can hardly be denied that it was impossible to separate resin from complex mixtures containing various kinds of fatty matters, with even an approximate degree of accuracy.

In 1882, however, Mr. T. S. Gladding introduced his excellent method for the determination of resin in various fatty substances, and it is with this method that my present remarks are chiefly concerned. Mr. Gladding described his method originally in the *American Chemical Journal* (Vol. III., No. 6.), and a full description will also be found in "Allen's Organic Analysis" (Vol. II., page 78, et seq.). The process in question is probably so well-known to most of you that it would be presumption on my part to dwell at length upon the *modus operandi*. I may say, however, for the benefit of any who may not be very familiar with the subject, that the method is based upon

the fact that silver resinate is soluble in ether containing a certain proportion of alcohol, while silver oleate, stearate, etc., are practically insoluble in such a menstruum. Three or four years ago, Alder-Wright and Thompson (*Chemical News*, Vol. 53, page 165), submitted Gladding's process to a careful investigation, with the result that, on the whole, they are satisfied with its essential accuracy. The main point upon which they differ from Gladding is with regard to the solubility of certain fatty silver salts, which they find in some cases to be greater, and in others less, than stated by Gladding in his original paper.

I have recently had a good deal of experience of Gladding's process as applied to the determination of resin in soap, and have found it very satisfactory. I find it best to work on the soap itself, instead of on the fatty acids separated therefrom, and have no difficulty in obtaining good results by slightly modifying the original process in one or two details, which will readily suggest themselves to anyone with a little practice. As I believe there is no record of experiments made with Gladding's process on soap containing known proportions of resin, the following results are interesting as confirming the accuracy of the method.

Some time since I received for analysis a sample of soap, in which an estimation of the resin was required. The firm who sent the soap knew approximately the percentage of resin present, but I was not aware until afterwards that this was a test case. I reported that the soap contained 30·7 per cent. of resin. One of the parties concerned subsequently informed me that he had calculated it to contain 30 per cent., so my estimation was considered very satisfactory. Since then, two of the largest soapmaking firms in this district have been so kind as to supply me with samples of soap containing moderate amounts of resin, at the same time informing me of the proportions of fatty matters and resin employed in the manufacture thereof. I was told that one of these samples, which I will term "A," had been made from a mixture of 100 parts tallow and twenty-five parts resin by weight, and the other, "B," from a mixture of seven parts fats (nature not specified) and two parts resin. Calculated from the percentages of mixed fatty and resin acids respectively present in the two soaps, the theoretical amounts of resin would be 12·84 per cent. in "A," and 13·82 per cent. in "B."

On examining the two samples by Gladding's method I found the following percentages of resin :—

|     |    |    |    | Found.          |    | Calculated.     |
|-----|----|----|----|-----------------|----|-----------------|
| "A" | .. | .. | .. | 13·17 per cent. | .. | 12·84 per cent. |
| "B" | .. | .. | .. | 14·06 „         | .. | 13·82 „         |

These results prove the reliability of Gladding's method, at any rate in the case of ordinary hard soaps.

It may be interesting to mention that I recently heard of a certain chemist (a well-known member of our Society) stating as the result of his analysis of a much advertised cheap soap, that it contained only about one-half the amount of resin which his clients knew to be present. This circumstance alone is, I think, sufficient to show that a little more light is desirable on methods employed for determinations of resin. If my paper to-night should prove the means of attracting more attention to this important matter, I shall feel amply repaid for bringing the subject before you.

# ON THE SOLUBILITY OF PHOSPHATE OF ALUMINA IN ACETIC ACID WITH SPECIAL REFERENCE TO THE ESTIMATION OF ALUMINA IN FLOUR, BREAD, ETC.

BY W. C. YOUNG, F.I.C., F.C.S.

(Concluded from page 63.)

·1 per cent. alum solution used :

|    | A.      | B.      | C.      | Mean. |         |
|----|---------|---------|---------|-------|---------|
| 1. | ·0215   | ·0235   | ·0235   | ·0228 | gramme. |
| 2. | ·0215   | ·0235   | ·0240   | ·0230 | "       |
| 3. | No ppt. | No ppt. | No ppt. |       | "       |
| 4. | ·0165   | ·0145   | ·0190   | ·0167 | "       |
| 5. | ·0205   | ·0150   | ·0200   | ·0185 | "       |

·2 per cent. alum solution used :

|    | A.      | B.      | C.      | Mean. |         |
|----|---------|---------|---------|-------|---------|
| 1. | ·0445   | ·0450   | ·0445   | ·0445 | gramme. |
| 2. | ·0460   | ·0465   | ·0465   | ·0463 | "       |
| 3. | No ppt. | No ppt. | No ppt. |       | "       |
| 4. | ·0235   | ·0225   | ·0230   | ·0233 | "       |
| 5. | ·0400   | ·0400   | ·0410   | ·0403 | "       |

These results show (except in experiment No. 1 with the ·1 per cent. solution of alum, where the quantity obtained was practically the same as when 5 c.c. of acetic acid were used) that the increase of acetic acid had a decided effect on the solubility of the phosphate of alumina, especially when precipitated in the cold, or when, after precipitation by boiling, it remained in contact with it in the cold for some hours.

In determining the quantity of alum present in adulterated bread or flour by Dupré's process or its modifications, there is present during the process either chloride of ammonium or sodium in addition to the salts used in these experiments, and as the former might possibly influence the precipitation of phosphate of alumina, I repeated the series of experiments, adding in each 10 c.c. of a 20 per cent. solution of chloride of ammonium, the result obtained being as follows :—

·1 per cent. solution of alum as before, with 5 c.c. acetic acid and 10 c.c. of a 20 per cent. solution of chloride of ammonium :

|    | A.      | B.      | C.      | Mean. |         |
|----|---------|---------|---------|-------|---------|
| 1. | ·0245   | ·0230   | ·0230   | ·0235 | gramme. |
| 2. | ·0250   | ·0250   | ·0250   | ·0250 | "       |
| 3. | No ppt. | No ppt. | No ppt. |       | "       |
| 4. | ·0215   | ·0215   | ·0225   | ·0218 | "       |
| 5. | ·0215   | ·0225   | ·0235   | ·0235 | "       |

·2 per cent. solution of alum as above :

|    | A.      | B.      | C.      | Mean. |         |
|----|---------|---------|---------|-------|---------|
| 1. | ·0475   | ·0485   | ·0485   | ·0482 | gramme. |
| 2. | ·0475   | ·0485   | ·0475   | ·0478 | "       |
| 3. | No ppt. | No ppt. | No ppt. |       | "       |
| 4. | ·0425   | ·0440   | ·0430   | ·0432 | "       |
| 5. | ·0450   | ·0465   | ·0455   | ·0457 | "       |



·1 per cent. solution of alum with 15 c.c. acetic acid, the rest as above :

|    | A.      | B.        | C.      | Mean. |         |
|----|---------|-----------|---------|-------|---------|
| 1. | ·0220   | ·0225     | ·0225   | ·0223 | gramme. |
| 2. | ·0245   | ·0245     | ·0235   | ·0242 | „       |
| 3. | No ppt. | No ppt.   | No ppt. |       |         |
| 4. | No ppt. | No ppt.   | No ppt. |       |         |
| 5. | ·0155   | Turbidity | ·0195   | ·0175 | „       |

·2 per cent. alum solution, the rest as in last series :

|    | A.      | B.      | C.      | Mean. |         |
|----|---------|---------|---------|-------|---------|
| 1. | ·0405   | ·0415   | ·0405   | ·0408 | gramme. |
| 2. | ·0425   | ·0415   | ·0445   | ·0428 | „       |
| 3. | No ppt. | No ppt. | No ppt. |       |         |
| 4. | No ppt. | No ppt. | No ppt. |       |         |
| 5. | ·0365   | ·0345   | ·0360   | ·0357 | „       |

From these results it will be seen that the addition of the chloride of ammonium to the experiments in which 5 c.c. of acetic acid were taken completely prevented the immediate precipitation in the cold in every case, lessened the amount of precipitate obtained after standing some hours, and increased the quantity dissolved by standing in the cold after precipitation by boiling, but had little effect upon the precipitation when collected immediately after boiling. In the experiments in which 15 c.c. of acetic acid were taken, the addition of chloride of ammonium completely prevented the precipitation in the cold, even after standing over-night, and materially lessened the precipitation in every other case.

My object in arranging the experiments in the manner described was to produce, as nearly as I could, the conditions existing in Dupré's method and the various modifications since suggested.

Dupré insists upon precipitation in the cold, using a small excess of acetic acid, Wanklyn precipitates boiling with a large excess of acetic acid, separating the precipitate immediately, and Bell boils and sets aside for several hours, using a small excess of acid.

The results of my experiments show that the nearest approach to the truth is obtained when the precipitate is separated immediately after boiling ; but it is generally admitted that by so doing some phosphate of calcium is obtained with the phosphate of alumina.

I have a strong opinion that the temperature has some influence upon the quantity of precipitate obtained in the cold, or when the precipitate has been allowed to stand in contact with acetic acid in the cold, after precipitation by boiling, and regret that I have not had time to put the matter to the test, but I have noticed that the quantity obtained in cold weather is less than in hot.

I may mention that rye bread, of which I frequently have samples for analysis from the east end of London, invariably gives a strong reaction with a logwood test, although I have never found more than ·008 gramme. phosphate of alumina in 100 grammes.

*(Conclusion of the Society's Proceedings.)*

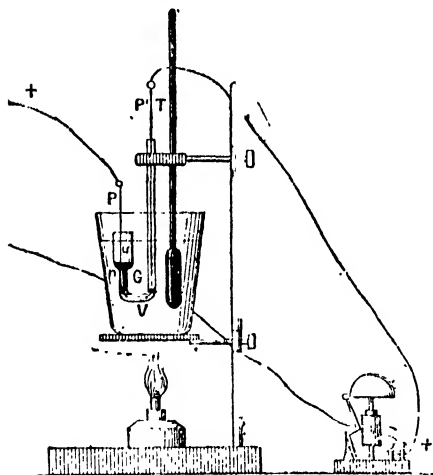
# METHODS AND APPARATUS IN USE AT THE LABORATORY OF THE BOURSE DE COMMERCE AT PARIS FOR THE ANALYSIS OF CERTAIN COMMERCIAL ORGANIC PRODUCTS.

By DR. MUTER.

SOME years ago we gave an account in the ANALYST of the methods in use at the Paris Municipal Laboratory, and we think that many of the readers of the journal will be interested to know how things are managed at the new laboratory of the Bourse, under the direction of M. Ferdinand Jean. Many of the methods and apparatus in use at this establishment are the invention of the director, and have the merit of the greatest ingenuity. This is specially noticeable in the analysis of fats and of tanning materials, with both of which subjects we propose to deal in the present article.

## (1) APPARATUS FOR TAKING THE MELTING-POINT OF FATS.

In this arrangement the melting-point of the fat is taken as being the degree at which it is sufficiently fluid to permit of the sinking down of mercury placed on the surface of the solid fat and the establishment thereby of an electric contact, which in turn rings a bell at the exact moment of contact. The drawing given herewith will



easily explain its action. The essential part is the "U" tube G (having the form shown) which is held, together with the thermometer T, in a vessel of water over a source of heat. The fat, having been melted at the most gentle possible heat, is poured into the "U" tube by the shorter limb so as just to fill the bend. Before it has time to solidify two platinum wires are pushed down so that a wire reaches well into the bend on each side, but the two wires do not quite touch each other. Some

mercury is now placed on the top of the solidified fat in the shorter limb, and the tube and thermometer are placed *in situ*. One of the platinum wires is then connected to one side of an electric bell, and the other

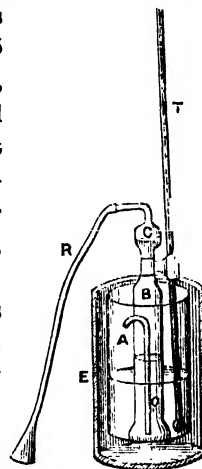
to one pole of a galvanic cell, the other pole of the cell being connected to the other side of the bell to complete the circuit. Heat is then cautiously applied and, at the moment of fusion, the mercury sinks, establishes contact, and the bell rings. The degree marked on the thermometer at the instant the bell rings is the melting-point of the fat. The apparatus is certainly very sensitive, and it is possible to act on samples of the same fat again and again, and obtain results that are exactly concordant. Of course, with such an arrangement, one must do as has been done in the laboratory and establish one's own standard for the melting-points, as the results will not always agree with recorded figures by the ordinary methods of taking melting-points. M. Jean lays the greatest stress on the necessity of always avoiding the fusion of fats to more than a degree or two over their melting-point before submitting them to examination, as he is a strong believer in the doctrine that fusion

of fats (especially of those like butter) completely alters their proximate molecular arrangement. He argues that many of the discordant results obtained by various observers of the physical properties of fats (such as density, melting-point, etc.) are entirely due to such rash and prolonged fusion before analysis.

In the analysis of tallows, palm oils, etc., the solidifying point of the fatty acids separated after saponification is considered a strong point. This is done in test tubes about 12 centimetres long and 15 millimetres in diameter, which are half filled with the fused acids, and a delicate thermometer (graduated in tenths of a degree) is introduced so that it goes well down into the tube but does not touch the bottom. This tube is placed in an outer jacket to prevent too rapid cooling, and the whole is watched. The thermometer sinks regularly at first until crystals of fatty acid begin to form on the surface and on the sides of the tube, and then, for a moment or two, the thermometer ceases to sink. At this point the fat is slightly agitated by turning the thermometer three times to the right and then three times to the left, when the temperature will be noticed to rise several tenths of a degree and then again become stationary. It is this latter point that is considered to be the true solidifying-point of the fatty acids, and the standards of tallow, etc., are set thereon.

## (2) APPARATUS FOR TAKING THE HEATING POWER OF OILS WITH SULPHURIC ACID.

The construction of this apparatus (called a thermelæometre by M. Jean) will be easily understood by reference to the illustration. A is a little glass cylinder having a graduation at the height of 15 c.c.; B is a specially constructed tube for containing the acid, having a perforated stopper connected to an india-rubber tube and mouthpiece. A little delivery tube is fused into its side, so that if the operator blows gently into the mouthpiece, Y, any fluid contained in the tube is ejected through the delivery tube at a regular rate of speed. T is a thermometer dipping into the oil cylinder, and E is a non-conducting outer casing to prevent the loss of heat. The acid used is a commercial acid of 1.819 specific gravity, which is kept in a large bottle fitted with one of M. Jean's automatic burettes, by which the acid can be measured into the apparatus without any exposure to the air, and in which it may be stored for any length of time without absorbing any moisture or decreasing in strength. To use the apparatus, 5 c.c. of acid are introduced into the inner tube and the stopper securely fixed. Fifteen c.c. of the oil are then placed in the cylinder, and the acid tube having been grasped by the hand, the oil is stirred thereby (applying heat or cold, as the case may be) until the thermometer marks 20° Centigrade. The whole is then placed in the outer non-conducting case, and, by blowing into the mouth-piece the acid is caused to mix with the oil (the acid tube and thermometer being meanwhile used as a stirring arrangement) until the thermometer marks its maximum. In the case of drying oils, 5 c.c. of a retarding mineral oil of .860 specific gravity are first added to the 15 c.c. of oil, and the effect of this addition is allowed for by the usual calculation. It is remarkable how handy this little piece of apparatus is, and what

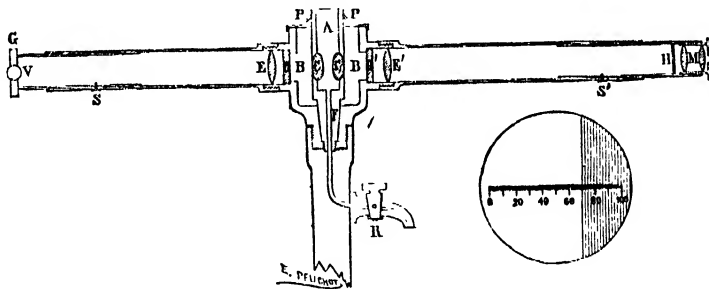


really concordant results can be obtained by its use time after time with different experiments on the same oil. If the oil to be examined be at all rancid, it is invariably shaken up several times with hot alcohol to remove free fatty acids and then run off from the separator in which the shaking was conducted and dried at  $110^{\circ}$  Centigrade. In actual practice all oils are really thus treated before taking their heating power, and where the oil is very stale indeed, it is saponified and the heating power of its fatty acids is taken, but in this case they begin working from the initial temperature of  $30^{\circ}$  Centigrade. In determining the nature of an oil or fat that has been already saponified (such as in a soap) the acids are liberated, dried at  $110^{\circ}$  Centigrade, and treated in the apparatus at the initial temperature of  $30^{\circ}$  Centigrade. There are, according to M. Jean, many oils showing very little difference on the original oil, but yet exhibiting marked differences when the process is applied to their fatty acids.

### 3. THE OLEOREFRACTOMETRE AND ITS USES.

The analysis of oils and fats is practically carried out by three observations: (1) the density; (2) the thermelæometre as above described; (3) by the important instrument with which we are now about to deal, the construction of which will be evident on studying the drawing.

The centre of the instrument is formed by a circular metallic receptacle, B B, closed by two opposite lenses, E E, from which extend two tubes, S S, the one ending in a collimator, G, and the



other in a short-visionsed telescope, M. In the middle of the receptacle is placed an inner metallic reservoir, A, having glass sides placed at a suitable angle, so as to form a prism. In front of the field-glass of the telescope is a photographic scale, H, and there is also a moveable vertical shutter, so placed as to divide the luminous field of the instrument into two parts, the one being quite bright, while the other is in shadow. It is the position of the edge of this shadow on the scale that determines the readings with the apparatus. If the same liquid be placed in both reservoirs the shadow will come on the zero of the scale; but if a different liquid be placed in the inner prismatic reservoir, the shadow will come at some point either to the right or to the left of the zero, according to the nature of the refractive power of the liquid. The appearance of the shadow in the field is shown in the drawing. The illumination is obtained by an ordinary gas jet placed opposite to the collimator end of the instrument. Both receptacles are furnished with draw-off cocks, and are enclosed in an outer case (not shown in the drawing), into which water is put for the purpose of regulating the temperature, and which case is heated by a little lamp placed underneath, so as to maintain its contents at any desired degree. M. Jean has invented a typical oil that gives no refraction, and with which the outer receptacle is always filled, and the

temperature is brought to 22° C. If now some more of this oil be also brought to 22° C, and placed in the prismatic reservoir, the shadow will mark zero, or if it does not do so it is adjusted to that point by moving the shutter. The typical oil is then run out of the prism, and the oil to be tested, having been brought to 22° C., is placed therein and the reading is taken. All the vegetable oils, and some marine animal oils, deviate the shadow to the right of the zero, while the terrestrial animal oils act in the contrary sense. It takes about half an hour to regulate the instrument and get all the temperatures equal in the reservoirs, but once this is attained, one sample after another can be done at intervals of five minutes, a portion of every sample of oil being used to rinse out the inner prismatic reservoir before actually filling it for observation. The following table will give some idea of the differences that can be got between the various vegetable oils:—

|            |    |    |    |   |         |   |      |
|------------|----|----|----|---|---------|---|------|
| Olive      | .. | .. | .. | + | 1.5 to  | + | 2    |
| Colza      | .. | .. | .. | + | 16.5 to | + | 17.5 |
| Ground-nut | .. | .. | .. | + | 4.5     |   |      |
| Sesame     | .. | .. | .. | + | 17.0    |   |      |
| Cotton     | .. | .. | .. | + | 20.0    |   |      |
| Castor     | .. | .. | .. | + | 40      |   |      |
| Linseed    | .. | .. | .. | + | 53      |   |      |
| Hempseed   | .. | .. | .. | + | 33      |   |      |
| Poppy      | .. | .. | .. | + | 30 to   | + | 34   |
| Almond     | .. | .. | .. | + | 6       |   |      |
| Japonica   | .. | .. | .. | + | 50      |   |      |

Of the terrestrial animal oils and fats which go to the left we have:—

|                     |    |    |    |    |   |      |
|---------------------|----|----|----|----|---|------|
| Neats-foot          | .. | .. | .. | .. | — | 3    |
| Horse-foot          | .. | .. | .. | .. | — | 12   |
| Lard                | .. | .. | .. | .. | — | 12.5 |
| Beef tallow         | .. | .. | .. | .. | — | 16   |
| Mutton tallow       | .. | .. | .. | .. | — | 20   |
| Butter fat          | .. | .. | .. | .. | — | 35   |
| Margarine (average) | .. | .. | .. | .. | — | 15   |
| Oleic acid          | .. | .. | .. | .. | — | 34   |

Before observing any oil, it is to be, if at all rancid, shaken up in a separator with hot alcohol, to remove the free fatty acids, and dried at 110° C. This is especially necessary in the examination of the lower qualities of olive oil, and indeed, with this particular oil, it is always desirable to proceed in this manner, if a preliminary examination of the oil itself does not indicate the proper refraction.

In applying the oleorefractometre to solid fats, such as butter and lard, it is necessary to work at 45° Centigrade. The butter is first melted at the lowest possible temperature and strained through muslin. It is then dissolved in ether, and the ethereal solution is shaken up in a separator with tepid water. The solution is then transferred to a flat-bottomed flask, the ether is distilled off, and the residual fat is slowly heated up to 110° C. till quite dry. Lastly, it is cooled down to 45° C and examined in the refractometre. Thus treated, butter gives a refraction of 35 to the left, while margarine gives an average of 15 in the same direction. M. Jean has met with exceptional butters from a single cow's milk in which the refraction has fallen to 33, but out of the immense number of samples examined annually in the laboratory, all the genuine butters come up

to the 35 with very few exceptions, and at the Bourse laboratory they consider that they can always certify with confidence to any amount of adulteration over 10 per cent. We tried to take an observation on some samples of exceptional butter fat given us by Dr. Vieth last spring; but they were entirely decomposed and came out nearly tallow. On the question of decomposition, the custom over there is to entirely refuse to give an opinion on a sample of butter unless it is quite fresh. The use of vegetable fats in the manufacture of margarine renders its detection by the instrument exceedingly easy, because the least quantity of such fat sends the refraction down tremendously. American lard adulterated with vegetable oils is very readily caught by the apparatus, because of the great variation in the refraction of lard ( $-12.5$ ) and that of cotton oil ( $+20$ ).

The use of the instrument is not, however, limited to the analysis of fats, but it is also employed for the detection of methylated spirit as follows:—Pure spirit, of exactly the same density as the sample to be examined, is put into the outer receptacle, and the inner one is also charged with the same spirit and the zero set. The standard spirit is run out of the prism and its place is filled with the sample, when a large left-hand deviation will be shown if methyl alcohol be present. Ten per cent. of methylation will show as much as 13 degrees. No mistake can be made between methylated and impure spirit, because the presence of fusel causes a refraction on the right.

The instrument is also employed in the analysis of oil of turpentine in a similar manner. It is first set with good oil of turpentine, and then the genuine is run out of the prism and the sample is substituted. The presence of either light oil of tar or of petroleum spirit, is at once shown by the powerful left-handed refraction produced. Thus, 10 per cent. of light oil of tar will produce a deviation of something like 40 degrees, while the same amount of petroleum spirit will deviate about 15.

M. Jean is now engaged on researches on the various essential oils employed in perfumery, and he has good hopes of soon placing chemists in a position to put a stop to the great amount of fraud that now exists in this trade, owing to the want of good processes and standards.

The whole working with this instrument is at the moment in its infancy, but I fancy it will one of these days become an indispensable adjunct to every commercial laboratory. At the present time its cost (£16) is somewhat prohibitory. It is made by Duboseq.

Before leaving the subject it will be interesting to state that the instrument has been put to the test by a committee of the French Agricultural Society. They had six samples made up of pure butter from various sources, and also of butter adulterated with margarine. These were examined by M. Jean in the presence of the Committee, and he was found to be correct in every case within ten per cent. of the admixtures, while all the pure butters were correctly recognised and duly passed as such.

Whatever be the cause of the varying refractive powers of oils and fats, it evidently does not vary with their density, because we find oils whose densities are very similar and which yet exhibit totally different refractions. It is this point that makes the joint determination of the density and of the refraction so useful. Supplement this with a really accurate determination of the heating power and, when necessary, with the Reichert and iodine process, and it would almost seem as if we were at last on our way to the real power of distinguishing between the various oils and fats.

*(To be continued.)*

DETECTION AND QUANTITATIVE ESTIMATION OF ORGANIC  
AND INORGANIC POISONS IN BODIES.

BY DR. ANTON SEYDA.

*(Continued from page 73.)*

THE following observations, which I have made during my search for alcohol in the various organs from persons who were confirmed drunkards, will be of interest. The organs did, however, not reach me for a week or a fortnight. 1. Pure ethylic alcohol was found in a few cases. From the contents of each jar containing respectively the stomach, duodenum small intestine; the pieces of the large glands of the abdomen; the lungs and brain, I have always succeeded in getting alcoholic distillates, but I never succeeded in getting alcohol or aldehyde from the urine. In many cases (it was not known whether the persons had partaken of alcoholic liquors shortly before death) I noticed the interesting fact, that whilst the distillate from the stomach was absolutely free from alcohol, the liver, kidneys, spleen, yielded a distillate containing it. In one case the reaction of the stomach was acid, and in the other faintly alkaline. The distillates when containing alcohol, gives the following reactions:—

1. Alkaline permanganate is reduced in the cold; the filtrate reduces ammoniacal silver nitrate.

2. A mixture of potassium bichromate with sulphuric acid is also reduced. The mixture has either the odour of aldehyde, acetic acid, acetic ether, or a pungent odour of rum, or often of a fruit essence.

3. A more or less strong iodoform reaction will be got.

4. If a few drops are collected at the beginning of the second distillation (over dry potassium carbonate), these will burn with the characteristic alcohol flame. This beautiful (but not very conclusive) test may even succeed when the organs are in an advanced state of putrefaction, but it will have to be conducted with great care, and best in a dark room. Before setting light to it, the crucible containing the spirit must be slightly warmed. The drawback to this test is the waste of the greater part of the spirit.

The cases where alcohol was only obtained from the liver and spleen, whilst none could be got from the stomach, etc., seem to me very peculiar. It is not improbable that the alcohol was formed by a kind of fermentation of the glycogen contained in the liver. It is also difficult to explain how it came that in one case where the medical men conducting the post-mortem, recognised alcohol by its smell, and certified as to alcoholic poisoning, no ethylic alcohol was found, but its higher homologues. This, however, was after a lapse of eight days between the inquest and the analysis. This strange fact may perhaps be explained by the great volatility of ethylic alcohol, causing it to evaporate even from the dead organism. The following experiments which I made to show the volatility of even dilute alcohol, proved interesting:—

In a beaker 75 m.m. square, I put some very dilute alcohol, and allowed it to spontaneously evaporate, estimating the percentage of alcohol from time to time by means of the vapourimeter. The results were as follows:—

On 20th December, 1886, the liquid contained 2·4 volumes of alcohol.

|                       |   |   |     |   |
|-----------------------|---|---|-----|---|
| " 21st                | " | " | 2·0 | " |
| " 24th                | " | " | 1·4 | " |
| " 27th                | " | " | ·75 | " |
| " 28th                | " | " | ·60 | " |
| " 10th January, 1887, | " | " | ·20 | " |
| " 22nd                | " | " | ·0  | " |

The beaker still contained water.

From these experiments it is plain that alcohol rapidly evaporates even from dilute solutions. If one now considers how clumsily post-mortems are sometimes conducted, it can scarcely be a matter of surprise, the alcohol has in many instances completely evaporated before the organs reach the analyst. In conclusion, I may mention that the largest quantity of alcohol I ever found in a stomach did not exceed ·2 gram., whilst the other organs yielded still less of that substance.

#### THE SECOND FRACTION.

##### (a) *Carbolic Acid.*

As this body is always among the products of the putrefaction of albumenoids, one will generally find a trace of it with Millon's reagent\* or (though not so frequently) with bromine water. If a poisonous dose is present, its amount may be estimated in a satisfactory manner as follows:—

The distillation is carried on until what passes over, gives no colouration with ferric chloride. Not to lose any, it is advisable to continue the distillation until no colouration is got by Plugge's test. Both distillates are now filtered off from any fatty matter, and separately shaken out with *pure* ether. The joint ether is now allowed to evaporate, and the residue is titrated in the well-known manner with bromine water and hypo.

##### (b) *Prussic Acid.*

Before applying any other test, I first use a strip of filter paper dipped first in a very weak solution of copper sulphate, and then in freshly prepared tincture of guaiacum. If the (tartaric acid) distillate contains prussic acid, the paper when moistened with it will turn blue. If no colouration is got, it is quite superfluous to try any other tests, but if obtained, it is as well to try and get the prussian blue, the sulphur and also the nitroprusside test. As regards the prussian blue test, I must emphatically warn against using too much ferrous sulphate as otherwise a yellow colour will almost completely obscure the blue. If the amount of prussic acid is very small, a precipitate will sometimes take a long time to form. When applying the sulphur test, the great thing is to avoid an excess of ammonium sulphide.

If prussic acid has been found, one must not neglect to test the residue in distilling flask for possible ferrocyanides.

A quantitative estimation of the prussic acid is conducted as follows:—The distillate is, if necessary, acidified with nitric acid, and precipitated with silver nitrate. The precipitate is collected on a weighed filter, washed, dried and weighed. To make sure, the precipitate is ignited and the residual silver also weighed.

\* Note by Translator. A solution of mercurous nitrate containing nitrous acid; first used by Professor Plugge for the detection of phenol and allied bodies.—L. de K.



(c) *Phosphorus*.

To observe very plainly the glowing of the phosphorus, I must recommend the use of the bulb-tube. The vapours for a long time condense in the bulb, which, in consequence, will appear quite luminous. If the phosphorescence vanishes, it may be several times made to again appear by opening the steam apparatus for a moment (and temporarily removing the flame) so as to let a little air get in. After distilling for about an hour, the distillation is stopped. All the while the receiver must have been kept very cool and also connected with a U-tube containing solution of silver nitrate. After particularly noticing whether there are any globules of phosphorus, the liquid may be tested for phosphoric acid by means of chlorine water and ammonium molybdate. A quantitative estimation may be attempted, but only about half the original phosphorus will, as a rule, be found. If no phosphorus has been detected, it must not be omitted to test the residue in retort for *phosphorous* acid, say by Dusart-Blondlot's process.

## ALKALOIDS AND ALLIED BASES.

The testing of organs for alkaloids is, as is well known, one of the most difficult chemical problems, which fact will be admitted by every analyst of long standing and experience. Our imperfect knowledge of the ptomeines, and the conditions necessary to their formation and disappearance, makes it so difficult to judge about the alkaloidal nature of a substance. There has already been such an amount of literature about ptoma-conine, ptoma-strychnine, etc., that I should not wonder to notice one of these days a pamphlet on the preparation of strychnine, morphine, etc., from putrefying white of egg. It is argued with much truth, that a nitrogenous base, isolated from organs, is only then to be pronounced a vegetable alkaloid when it possesses *all its physical, physiological and chemical properties*. Of course, in such a case, there is no fear of its being a ptomeine; but alkaloids are generally present in such small quantities, that it is mostly impossible to get *all* reactions satisfactorily, and I feel sure that many a too-particular analyst has in consequence been induced to call vegetable alkaloids ptomeines.

It certainly is much easier, in the present state of science, to pronounce a residue to be a ptomeine instead of an alkaloid, for the simple reason that one rarely ever succeeds in isolating the base from the organs in a *perfectly pure condition*.

The best way to extract the alkaloids is by means of a alcoholic solution of tartaric acid. The fat which separates out scarcely deserves any further attention, although it is not quite impossible that it may act as a solvent for organic poisons;\* but it mostly consists for the greater part of cholestérin. The extracts got from a stomach are mostly of a bright yellow colour, more particularly if there was an abundance of bile; but organs containing much blood give extracts of a much darker colour, and should therefore be analysed separately.

A clarification of the solution may be attempted by adding alcoholic solution of tartaric acid as long as a precipitate forms. The filtrate is evaporated, the residue taken up with water, and then nearly neutralised with potash. On adding alcohol,

\* For instance, nitroglycerine. In the absence of fatty matter, this is best isolated by extracting the air-dried substance with chloroform, finally drying the extract over sulphuric acid.

the potassium tartrate is precipitated, carrying down a good deal of the colouring matter.

After evaporating off the spirit, the watery fluid is once more tested as to its reaction, and, if necessary, neutralised with potash. As it is difficult to get perfect neutrality, it is best to use very delicate litmus paper, working until only the faintest acidity is noticed. Before using the regular course, one must never omit to test a little of the solution for meconic acid, and also to notice its behaviour towards iodic acid. If no iodine is liberated (acidify the fluid with tartaric acid), it is no use trying for morphine; but of course a separation of iodine does not in the least prove the presence of that alkaloid, as other bodies may cause the reaction. The fluid is now divided into three parts. Part 1 is made alkaline with potash and distilled in a current of steam or hydrogen. The distillate is to be especially tested for nicotine, conine, and aniline, which is done best by first shaking it with ether and evaporating this in a current of air, the flask containing the solution being surrounded with water of 70—80°C. When about 10 c.c. of ether are left, it is put to spontaneously evaporate in a small beaker. The residue is dried in vacuo over sulphuric acid, and then made into a neutral hydrochloride.\* If necessary, the usual tests for nicotine may be supplemented by preparing the double salts with gold or platinum chloride, and submitting these to a quantitative analysis.

If no volatile bases have been found, the second portion is shaken out: 1. With ether, both from acid and alkaline solution. 2. With chloroform from alkaline solution. 3. With amyl alcohol after addition of ammonium chloride, but this is only necessary if the iodic acid test has been successful. Before shaking with the chloroform, any ether must be expelled by gentle warming and blowing, and before using the amyl alcohol, any chloroform must be likewise got rid of.

If reactions are got which point to the presence of a particular alkaloid, a special process is applied to the third part of the fluid. It is a good plan to add solution of mercuric chloride, which precipitates every trace of nitrogenous base in twenty-four hours. The deposit is washed with a weak solution of sublimate, and the alkaloid is then isolated in the usual manner. The residues left after evaporation of the ether, chloroform, and amyl alcohol must always be dried over sulphuric acid; they are partially amorphous and crystalline, colourless, or of a yellow or brown colour. Froehde's reagent is often reduced with a blue colour, to which, however, not much importance must be attached. The same may be said of the passing green colour obtained with a sulphuric acid solution of ammonium vanadate. The residue from the alkaline ether will nearly always get violet on warming with syrupy phosphoric acid, although this test has been supposed to be characteristic for aconite only.† The otherwise so splendid atropine test of Vitali (treating the pure alkaloid, first with fuming nitric acid, and then with alcoholic potash) will, however, mostly fail with the impure residue. The same failure is sure to occur on applying the chromic acid test (getting an agreeable odour).

\* Conine hydrochloride is of characteristic appearance.

† Note by Translator. I have often seen syrupy phosphoric acid turning violet on heating, most likely caused by some organic matter.

As a test for strychnine, ammonium vanadate has lately been strongly recommended and found trustworthy. The experiment is best performed in two ways. First of all, the solution of the vanadate in sulphuric acid is dropped on to the alkaloidal residue; and, secondly, solid vanadate is first added and the whole moistened with sulphuric acid. This test is preferable to the time-honoured test with bichromate, at least, when the alkaloid is somewhat coloured.

I must now call attention to an important fact, as far as I am aware, not yet published, viz.: Colocynth resin gives with vanadate solution a reaction almost like strychnine.

If this drastic (colocynth) is suspected, I proceed as follows:—The residue is mixed with a pinch of powdered bichromate with addition of a few drops of dilute sulphuric acid (1-2). At a little distance a little strong sulphuric acid is placed, and the two liquids drawn together with a glass rod. A beautiful violet-red is thus obtained, which gradually increases in colour. If vanadate is used instead of bichromate a blue colour is first obtained and a violet-red afterwards.\*

The residue obtained by evaporation of the amylic alcohol (which must first be passed through a dry filter) is often impure, and is best purified by treatment with alcohol. The morphine is then tested for by the ordinary reagents, or it may be tested after conversion into apomorphine.

#### METALLIC POISONS.

I either use the residue from the distillation or the residue from the extraction with alcohol, in which case the latter is expelled by gentle heat. After adding boiling water and a sufficiency of potassium chlorate, hydrochloric acid is gradually added until the organic tissues are disintegrated. I am sorry to say I cannot recommend Jeserich's plan of using chloric acid, as this seems never to be quite free from arsenic, otherwise it is an excellent process. After warming for some time to expel chlorine, if necessary with an occasional addition of hot water, a little tartaric acid is added to keep up any antimony, and the whole set aside for twenty-four hours.

##### (a) *The insoluble portion.*

This is collected on a filter and washed with water until the washings are colourless (if there should be a large residue, it is a good plan to once more treat with chlorine), then with alcohol, and finally (in a beaker) with ether, until the fat is practically removed. The residue is now burnt in a porcelain dish. The ash is first digested with weak hydrochloric acid and the insoluble ash collected, washed, dried, ignited, and weighed. If it should not merely look like sandy matter, its nature must be investigated, best by fusing it with (previously ignited) sodium hydrocarbonate in a platinum crucible. After treating the mass in water, any insoluble matter is dissolved in nitric acid, and the solution tested with hydrochloric acid (silver), sulphuric acid (lead, barium, strontium), and hydrogen sulphide. The alkaline filtrate is mixed with excess of hydrochloric acid and evaporated to dryness (to render silica insoluble). After taking up with acid water and filtering, the liquid may be tested for alumina. In a case of poisoning by barium chloride, where sodium sulphate had been given as an antidote, I

\* Note by Translator. This is very nearly the same as with strychnine, showing, after all, the advisability of always using the chromate reaction when testing for strychnine.

could not find any barium in the stomach, œsophagus, and duodenum, but got as much as .158 gram. of barium sulphate from the abdominal glands, brains, and lungs, whose joint weight was 719 grammes.

(b) *The soluble portion.*

I must state that it is absolutely necessary the fluid shall contain no free chlorine. After making up to a definite bulk, say 500 c.c., aliquot parts are taken and submitted to analysis.

(a)

Fifty to 100 c.c. are nearly neutralised with caustic potash in a porcelain dish, a small coil of clean brass is introduced, and the whole warmed for fifteen minutes. The coil is then washed with water, alcohol, and ether, and after drying (in desiccator) introduced in a combustion tube partly filled with coarse oxide of copper, and drawn out so as to be connected with two capillary tubes. By means of an aspirator a slow current of dried air is drawn through and the tube heated as if an elementary analysis were conducted. Any mercury will condense inside the capillary tubes.

Whilst still hot a drop of water is put on the combustion tube (close to the capillary one) and is so made to break. A minute particle of iodine is now introduced, and with the application of a gentle heat, its vapour mixed with the air current, is made to act on the mercury globules, which will then cause the formation of the characteristic mercuric iodide. As regards this very reliable process, I want to observe that a long immersion of the brass is not advisable because it gets too thickly coated with organic matter.

The quantitative estimation of the mercury I conduct as follows:—Through the hot acid solution, I pass hydrogen sulphide, and collect the precipitate on an asbestos filter. After washing with strong hot hydrochloric acid, the asbestos is rinsed into a beaker and digested with a few drops of nitric acid, which will soon dissolve out the mercury. After filtering through the same asbestos the mercury is precipitated as mercurous chloride by the addition of excess of phosphorous acid, which is allowed to act for twenty-four hours.

(b) *Antimony.*

Fifty c.c. of the liquid are put into a clean platinum dish, the excess of acid neutralised with ammonia, and a piece of pure zinc is introduced. After acting for six hours, the liquid is poured off and the antimony will have blackened the platinum, or, if much was present, deposited itself as a spongy mass. The liquid may contain traces of it, as antimony is somewhat soluble in concentrated solution of zinc chloride. Its quantitative determination is conducted as follows:—Though the hot fluid I pass hydrogen sulphide until the liquid has got cold. After standing for three days, the excess of hydrogen sulphide is removed by a rapid current of carbonic acid, a little ether being, if necessary, added to prevent frothing. The precipitate is filtered off and washed with a weak solution of ammonium acetate. It is then rinsed from the filter with solution of caustic soda, which is then saturated with hydrogen sulphide, which will cause the antimony to dissolve. After filtering off from any insoluble matter, the liquid is slightly acidified with hydrochloric acid and heated to boiling. After standing for a day, the precipitate is filtered off, washed, and finally oxidised with nitric acid. To completely get rid of

organic matter, the mass is made alkaline with caustic soda, dried and fused with a mixture of nitrate and carbonate of soda. The mass is now exhausted with proof-spirit, and the insoluble sodium antimoniate washed with proof-spirit to which a few drops of sodium carbonate have been added. It is then digested in a mixture of hydrochloric and tartaric acids, the liquid nearly neutralised with ammonia, and once more precipitated with hydrogen sulphide. The precipitate, which should now possess the characteristic colour of antimony sulphide, is not weighed as such, but I prefer to make it into oxide by treatment with fuming nitric acid, taking all precautions as advised by Bunsen.

To make sure of the absence of tin, I place the uncovered crucible in the reduction flame of a powerful burner, when the antimony will gradually, but completely volatilise.

*(To be continued.)*

## METHODS FOR DETECTING OLEO IN BUTTER AND COTTON SEED OIL IN LARD.

BY THOMAS TAYLOR, M.D., MICROSCOPIST, UNITED STATES DEPARTMENT OF AGRICULTURE.

*Abstract of paper read before the Chemical Society of Washington, D.C., March 13th, 1890.*

### TO DETECT OLEO IN BUTTER.

[I believe that this method will prove useful for all practical purposes under the oleomargarine laws of the United States.]

Dissolve in 20 c.c. of petroleum benzine 140 grains of a mixture of oleo and butter. Heat slightly to secure a perfect solution of the fats. Caseine and animal tissues may be removed by filtering the liquid while it is warm. Fill a test-tube with the filtered solution and place it in ice-water. In from five to twenty minutes the oleo fat will separate from the butter fat, and falls to the bottom of the tube, being sparingly soluble in cold benzine, while the butter fat remains in solution in cold benzine. Separate the oleo fat from the liquid butter by filtration. The fat recovered may be solidified by mechanical pressure, placing it between several layers of filtering paper to absorb the remaining benzine, after which the sheet of solid oleo may be removed from the paper with a palette-knife. The butter may be recovered by evaporating the benzine by means of heat.

### TO DETECT COTTON SEED OIL IN LARD.

Dissolve in 20 c.c. of petroleum benzine 140 grains of a mixture of lard and cotton seed oil. Heat slightly to secure a perfect solution of the lard. Remove animal tissues by filtering as above. Fill a test-tube with the filtered solution and place it in ice-water. The fat will be precipitated, and falls to the bottom of the tube by reason of its comparative insolubility in cold benzine, while the cotton seed oil remains in solution. Separate the lard from the cotton seed oil by the use of filtering paper, and subject the recovered fat to pressure as in the case of butter and oleo, by which means the remaining benzine is absorbed. The solidified fat may be removed from the paper with a palette-knife. The benzine is separated from the cotton seed oil by means of heat.

## ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

*(Continued from page 78.)*

## MERCURY FROM NICKEL.

With these two metals the current was allowed to act for sixteen hours. The results are as follows:—

|   | Mercury present in grams. | Nickel present. | KCN in grams. | Total dilution. | Current strength in c.c. O-H gas per minute. | Mercury found. | Difference in per cent. from the theoretical. |
|---|---------------------------|-----------------|---------------|-----------------|--|----------------|---|
| 1 | 0.2440                    | 100 per ct.     | 4½            | 200 c.c.        | 0.4 c.c.                                     | 0.2435         | -0.20 per cent.                               |
| 2 | "                         | "               | "             | "               | "  | 0.2432         | -0.32 "                                       |
| 3 | "                         | "               | "             | "               | "  | 0.2425         | -0.60 "                                       |

## MERCURY FROM COBALT.

Our experience with these two metals was so unexpected that we append the poor as well as the good results which were finally obtained:—

|   | Mercury present in grams. | Cobalt present. | KCN in grams. | Total dilution. | Current in c.c. O-H gas per minute. | Mercury found. | Difference in per cent. from the theoretical. |
|---|---------------------------|-----------------|---------------|-----------------|-------------------------------------|----------------|---|
| 1 | 0.2440                    | 100 per ct.     | 4½            | 200 c.c.        | 0.4 c.c.                            | 0.2386         | -2.21 per cent.                               |
| 2 | "                         | "               | "             | "               | "                                   | 0.2388         | -2.13 "                                       |
| 3 | "                         | "               | "             | "               | "                                   | 0.2364         | -3.11 "                                       |
| 4 | "                         | "               | "             | "               | "                                   | 0.2333         | -4.00 "                                       |
| 5 | "                         | "               | "             | "               | "                                   | 0.2366         | -3.02 "                                       |

The current acted for sixteen hours upon reducing the quantity of cobalt, and operating with the conditions, in other respects, the same as before (except in 11 and 13), we obtained:—

|    | Mercury present in grams. | Cobalt present. | KCN in grams. | Total dilution. | Current in c.c. O-H gas per minute. | Mercury found | Difference in per cent from the theoretical. |
|----|---------------------------|-----------------|---------------|-----------------|-------------------------------------|---------------|--|
| 6  | 0.2440                    | 75 per ct.      | 4½            | 200 c.c.        | 0.5 c.c.                            | 0.2353        | -3.56 per cent.                              |
| 7  | "                         | "               | "             | "               | 0.86 c.c.                           | 0.2357        | -3.40 "                                      |
| 8  | "                         | 50 per ct.      | "             | "               | 0.5 c.c.                            | 0.2387        | -2.25 "                                      |
| 9  | "                         | "               | "             | "               | "                                   | 0.2381        | -2.33 "                                      |
| 10 | "                         | "               | "             | "               | 0.86 c.c.                           | 0.2321        | -4.80 "                                      |
| 11 | "                         | 25 per ct.      | 3             | "               | 0.5 c.c.                            | 0.2442        | +0.09 "                                      |
| 12 | "                         | "               | 4½            | "               | 0.86 c.c.                           | 0.2342        | -4.01 "                                      |
| 13 | "                         | 12½ per ct.     | 3             | "               | 0.5 c.c.                            | 0.2445        | +0.20 "                                      |

Inspection of these figures discloses the fact that nothing approaching a separation of the two metals appears probable until in experiment (11), where not only the quantity of cobalt is reduced, but also that of the potassium cyanide. The result is then surprisingly close (+0.09 per cent.). This would seem to be due rather to the reduction of the quantity of cyanide, inasmuch as by its increase in experiment (12), we again have a minus error of 4.01 per cent., and in experiment (13), by reducing the quantity of cyanide to 3 grams., the result is satisfactory. As the quantity of cobalt in this instance was but half of that in experiment (12), the favourable result might be attributed to this. Hence the following trials were made:—

|    | Mercury present in grams. | Cobalt present. | KCN in grams. | Total dilution. | Current in c.c. O-H gas per minute. | Mercury found. | Time of precipitation. | Difference in per cent. |
|----|---------------------------|-----------------|---------------|-----------------|-------------------------------------|----------------|------------------------|-------------------------|
| 14 | 0.2250                    | —               | 3             | 200 c.c.        | 0.5 c.c.                            | 0.2250         | 16 hrs.                | —                       |
| 15 | "                         | 25 per ct.      | "             | "               | "                                   | 0.2256         | "                      | +0.26 per ct.           |
| 16 | "                         | 50 "            | "             | "               | "                                   | 0.2258         | "                      | +0.35 "                 |
| 17 | "                         | 75 "            | "             | "               | "                                   | 0.2258         | "                      | +0.35 "                 |
| 18 | "                         | 100 "           | 2.2           | "               | "                                   | 0.2235         | "                      | -0.60 "                 |

Cobalt was not found in the mercury deposit, nor mercury in the cobalt solution.

Evidently the quantity of cyanide present exercises a marked influence upon the separation. Returning to the separation of cadmium from cobalt, it will be observed that the amount of cyanide present there was 4½ grams., while the quantity of metal was less; yet the separation proved satisfactory.

#### SILVER FROM COPPER.

It yet remains for us to record some experiments upon the separation of these two metals in cyanide solution. Reference to a former paper (*American Chemical Journal*, 11, 264, and *Journal of Analytical Chemistry*, 3, 254) will show that our attempts in this direction were at that time fruitless. It was after the successful separation of cadmium from copper in cyanide solution that we were impressed with the idea that the separation of silver from copper ought to occur, since silver deposits so readily, even when exposed to a very feeble current. In the communication to which we refer, the current strength recorded was 1 c.c. O-H gas per minute. Since it was by carefully reducing this in other cases that we obtained good separations, we instituted a new series of experiments with silver and copper, acting upon the mixture with a much weaker current:—

|   | Silver present in grams. | Copper present. | KCN in grams. | Total dilution. | Current in c.c. O-H gas per minute. | Time in hours. | Silver found. | Difference in per cent. |
|---|--------------------------|-----------------|---------------|-----------------|-------------------------------------|----------------|---------------|-------------------------|
| 1 | 0.1788                   | —               | 4½            | 200 c.c.        | 0.10 c.c.                           | 16             | 0.1792        | +0.22 per ct.           |
| 2 | "                        | —               | "             | "               | 0.23 "                              | "              | 0.1788        | —                       |
| 3 | "                        | 100 p. c.       | "             | "               | 0.15 "                              | "              | 0.1788        | —                       |
| 4 | "                        | "               | "             | "               | 0.30 "                              | "              | 0.1787        | -0.05 per ct.           |
| 5 | "                        | "               | "             | "               | 0.20 "                              | "              | 0.1784        | -0.20 "                 |
| 6 | "                        | "               | "             | "               | " "                                 | "              | 0.1782        | -0.33 "                 |
| 7 | "                        | "               | "             | "               | 0.40 "                              | "              | 0.1783        | -0.28 "                 |
| 8 | "                        | "               | "             | "               | 0.15 "                              | "              | 0.1800        | +0.60 "                 |

We next dissolved 0.1732 gram. pure metallic silver in nitric acid. To its solution, after evaporation, there were added 100 per cent. copper and  $4\frac{1}{2}$  grams. potassium cyanide. On electrolysing, with a current of 0.15 c.c. O-H gas per minute, the resulting silver weighed 0.1725 grams. The latter contained no copper, nor could silver be detected in the copper solution.

A silver ten-cent piece, weighing 1.2236 grams, was brought into solution and diluted to 100 c.c. Of this solution two portions (25 c.c. each) were electrolysed in the presence of  $4\frac{1}{2}$  grams. potassium cyanide, with a current of 0.4 c.c. O-H gas per minute. The silver found was in—

- (a) 89.64 per cent.
- (b) 89.56 per cent.

Two silver determinations made with another coin gave :—

- (c) 89.44 per cent.
- (d) 89.44 per cent.
- (To be continued.)

#### LAW NOTES.

TWO CONVICTIONS FOR THE SAME SAMPLE OF MILK.—Mr. B. S. Weston, Sanitary Inspector for St. Matthew, Bethnal Green, submitted a sample of milk purchased from the Farmers' Direct Supply Association to the Public Analyst, Mr. A. W. Stokes, F.I.C. A certificate was returned stating the milk contained 10 per cent. of added water, and that 33 per cent. of the cream had been abstracted from the sample. Two summonses were taken out, one under section 6 and one under section 9 of the Adulteration Act. On February 28th, at Worship Street, Mr. Bushby heard the case. The defendant appeared by his Solicitor (Mr. Young), but the case was given against him, and a fine of £5 was imposed for the abstraction of the cream and £2 for the addition of water, costs being given in both cases.

#### REVIEWS, NOTES, ETC.

JOURNAL OF THE ROYAL AGRICULTURAL SOCIETY.—We have received the first number of the new series (the third) of this journal. It is to be issued quarterly, and being well printed and containing much that is vitally important to all agriculturists, it should certainly be appreciated by all interested in the subject. We observe very interesting reports from the society's consulting naturalist, and also from the botanist; while the analyst exposes a series of frauds in feeding meals, adulterated samples of which seem to be very prevalent of late.

EXERCISES IN PRACTICAL CHEMISTRY; AN INTRODUCTION TO QUALITATIVE AND QUANTITATIVE ANALYSIS, BY DR. W. R. HODGKINSON, F.R.S.E. London: George Kenning, Great Queen Street.

THIS is a little brochure in pamphlet form of 64 pages, giving the usual reactions and tests of the various metals and acids, and a few of the gases, with tables for quantitative analysis. It possesses no special feature, but is well and concisely put. Like many books of its class, it is, in our opinion, sorely deficient in a really systematic acid course, too much being left to the student's initiative in this matter. So far as qualitative work is an introduction to quantitative, then the title is correct, but we have looked in vain for any other attempt to explain quantitative analysis.



**SUGAR REAGENT.**—Matthieu-Plessy recommends the following as a reagent for cane-sugar, grape-sugar, and pyrogalllic acid: 54 pts. of ammonium nitrate are fused, and 34 pts. lead nitrate and 21 pts. of plumbic hydrate are added. The reagent melts at 105° C., and with the substances named gives mixtures, having in the presence of glucose a cherry red, with cane-sugar a coffee-coloured, and with pyrogalllic acid a chrome-green colour. — *Am. Journ. Pharm.*

**CHEMICALLY PURE SULPHATE OF QUININE** may be distinguished from the commercial sulphate and the sulphates of cinchonine, cinchonidine and quinidine by a solubility test in a mixture of chloroform and petroleum ether. 0.2 gram. are briskly agitated with a mixture of 30 parts by volume of petroleum ether (sp. gr. 0.680) and 70 parts chloroform, filtering and adding 3 to 4 volumes of petroleum ether; in the absence of the other sulphates the solution will remain clear. An admixture of only 0.1 per cent. other sulphate will give rise to a precipitate or turbidity. — (E. Hirschsohn.)

**SALT REGAL.**—This attractive effervescent saline, which has attained a high reputation on the Continent, the Colonies, and India, is, we are informed, about to be energetically pushed in this country. It should do well, because it is an original idea, and has been certified by Dr. Paul and several other analysts as being perfectly pure in all its ingredients. It is the only attempt that has yet been successfully made to combine an aperient with an active oxidising disinfectant without decomposing the latter, and is, therefore, chemically interesting to that extent.

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# THE ANALYST.

JUNE, 1890.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL meeting of the Society was held at Burlington House, on Wednesday 14th ult., the President, Mr. Adams, in the chair.

The minutes of the last meeting were read and confirmed.

On the ballot-papers being opened it was announced that Mr. W. Droop Richmond was elected as a member.

The following gentlemen were proposed for election :—As member, Mr. S. J. Steel, Chemist to Messrs. Martineau and Sons. As associate, Mr. T. H. Pearman, Assistant to Mr. A. H. Allen.

The following paper was read by the President, "Remarks on the Bitter of the Hop as Differing from the Bitter of Quassia and other Hop Substitutes."

The reading of the paper and the subsequent discussion extending to a late hour, the other papers announced to be read were necessarily postponed.

The next meeting of the Society will be held at Burlington House on the 11th inst.

*(Conclusion of the Society's Proceedings)*

## ON THE ANALYSIS OF PEPTONES.

BY M. ALPHONSE DENAEYER, BRUSSELS.\*

At the last meeting of the Association I had the opportunity, gentlemen, of drawing your attention to the analogies of reaction which peptone and gelatine present; and I insisted on the fact that in the analysis of the peptones of commerce, the gelatine, which in the meat peptones is due to the transformation of the tendinous parts of the

---

\* *Bulletin de l'Association Belge des Chimistes*, March 31, 1890.

muscular tissue, was precipitated by phospho-tungstic acid, as well as the real peptone of albumen and the albumose. The gelatine contains nitrogen, and therefore in the application of the König process for the determination of peptones, the gelatine is inevitably precipitated as well as the peptone, and the estimation of nitrogen under these conditions gives an important excess of peptone.

M. Bruylants said in the last discussion we had on the question, that the double iodide of potassium and mercury which I showed to be distinctive of albumose, peptone, and gelatine, was perhaps the basis of a system of separation of these bodies. The late hour of the meeting prevented my presenting to you the whole results of my researches on this point, and the application which I had already made of the reagent in the separation of these compounds. Keeping in mind the ideas I have expressed as to basing the operations of estimation on the rational preliminary separation of gelatine, albumose, and peptone, I use for the analysis of preparations of peptones the technical processes which I am about to show you. They are different from those suggested by König, but I think that elements for discussion and experiment will be found in them which will lead, perhaps, to new improvements.

#### METHOD FOR THE ANALYSIS OF PEPTONE PREPARATIONS.

The composition of these preparations always approximates to that of the albuminoids from which they have been derived by the action of the gastric juice. The constituent elements which it is necessary to determine in the analysis of peptones are the following:—1. Water. 2. Ash. 3. Insoluble matters, if any. 4. Gelatine. 5. Albumose. 6. Peptone. 7. Definite compounds. Among these elements we must remark that insoluble gelatine and the defined compounds may be absent.

*Water.*—The proportion per cent. is determined by evaporating in a water-bath some grammes of peptone. The complete desiccation is continued in an oven at 100° C. The residue is weighed after standing in vacuo over concentrated sulphuric acid for twenty-four hours.

*Ash.*—The residue previously dried is ignited and weighed accurately.

*Insoluble matter.*—The peptone is diluted with water, the insoluble residue is collected on a tared filter, washed with water, dried in the oven at 100° C., and weighed after cooling under the desiccator.

*Gelatine.*—The estimation is founded on its precipitation by ammonium sulphate; but as the albumose is also precipitated by this reagent, it is necessary, as a preliminary, to separate this compound. For this purpose I employ iodide of potassium and mercury, using Mayer's formula:—

|                     |    |    |    |                 |
|---------------------|----|----|----|-----------------|
| Iodide of potassium | .. | .. | .. | 49.801 grammes. |
| Chloride of mercury | .. | .. | .. | 13.546 „        |
| Distilled water     | .. | .. | .. | 1,000.000 „     |

A known weight of peptone, 1 or 2 grammes, dissolved in water, is precipitated by an excess of the reagent. After filtration and washing, the liquors are evaporated to a few cubic centimetres, then an excess of ammonium sulphate in saturated solution is added. The mixture is brought to the boiling point, which causes the coagulation of the gelatine against the sides of the vessel. When quite cold, the liquid is decanted, and the gelatine

washed first with ammonium sulphate, then rapidly with cold water, and finally with boiling alcohol, which removes the double iodide of potassium and mercury entangled by the precipitate. The gelatine remains adhering to the glass; the vessel is then dried in the oven and weighed. The gelatine still retains some ammonium sulphate, *which it is necessary to deduct from the weight obtained.* For this purpose the coagulum is dissolved in warm water, an excess of hydrochloric acid is added, it is filtered, and the filter washed with as little distilled water as possible. The ammonium sulphate is titrated in solution by a normal solution of chloride of barium, the end of the reaction being ascertained by filtering small portions to which drops of barium chloride are added.

One c.c. of normal chloride of barium containing  $\frac{120}{1000}$  of crystallised salt represents 0.08 gramme of ammonium sulphate.

*Albumose.*—One or two grammes of peptone are taken and dissolved in 5 c.c. of distilled water. An excess of ammonium sulphate is added to the clear solution. This reagent precipitates the albumose and gelatine if any are present. The precipitate is collected on a tarred filter. This is washed with solution of ammonium sulphate, dried and weighed. The precipitate is then dissolved in a sufficient quantity of hot water, and after filtration the ammonium sulphate is estimated by the process described above. From the weight of the precipitate obtained is deducted (1) the weight of the gelatine; (2) the weight of the ammonium sulphate; the difference giving the weight of the albumose.

*Peptone.*—One or two grammes of peptone are taken as before. The peptone is then dried in vacuo at 60° C., which produces great inflation of the mass. The porous residue is washed with alcohol at 95° in order to eliminate creatine, creatinine urea, sarcosolactic, formic, acetic and butyric acids, which are especially found in peptones prepared directly from meat. These compounds can be estimated in mass by evaporation of the alcohol. The residue is taken up by some grammes of water, and an excess of a solution of phosphotungstate of soda thus prepared is added

|                                   |             |
|-----------------------------------|-------------|
| Tungstate of soda .. ..           | 50 grammes. |
| Boiling distilled water .. ..     | 1000 "      |
| Phosphoric acid (medicinal) .. .. | 100 "       |
| Pure hydrochloric acid .. ..      | 150 "       |

*This last acid must be added after the solution is cold. The liquid is filtered after standing for twenty-four hours.*

This reagent precipitates the gelatine, the albumose and the peptone. After settlement a small portion of the clear liquid is tested, then the greater part of the solution is decanted and the precipitate is thrown on a Schleicher's filter carefully tared. The precipitate is dried in the oven, weighed after cooling in the desiccator, and the weight noted.

The precipitate is then introduced into a porcelain capsule and ignited in a gas muffle to total incineration of the organic matter and filter. This last residue is weighed and its weight, minus the weight of the filter ash, is deducted from that of the dry precipitate. The difference represents the weight of the peptonic matter precipitated. From this is deducted (1) the weight of the gelatine; (2) the weight of the albumose. The last difference gives the weight of the peptone.

This method gives results as accurate as those based on the determination of peptone by the estimation of nitrogen, and it has the advantage of being much quicker. Comparative analyses of eight samples of different peptones have given results differing but slightly from those obtained by calcination.

*Definite Compounds.*—Under this denomination are included the nitrogenous bases and the fatty and amido acids of muscular tissue.

The definite compounds are divided into nitrogenous and non-nitrogenous substances. Some are soluble and others insoluble in alcohol. Taking this classification I group them in the following order: Substances soluble in alcohol:

*Nitrogenous*: Creatine, creatinine urea.

*Non-nitrogenous*: Sarcolactic, formic, butyric, and acetic acids.

These substances may easily be determined collectively by evaporation of the alcoholic solution obtained by washing the product yielded by evaporation to dryness in vacuo before the precipitation of the peptone by phosphotungstate of soda. Substances insoluble in alcohol:

*Nitrogenous*: Taurine.

*Non-nitrogenous*: Inosite, dextrin, glycogen.

The proportion of these elements in the preparation of the peptone analysed is determined by difference.

I have applied my method of analysis to several commercial preparations of peptone as well as to the peptones specially prepared by myself. It is executed with perfect regularity. The following are three results selected from among the numerous applications which I have made of the method. They bear on the principal types of peptone preparations.

| Designation.               | Peptone of<br>purified<br>meat-albumen. | Peptone<br>of<br>egg-albumen. | Peptone<br>direct from<br>meat. |
|----------------------------|---|-------------------------------|---------------------------------|
| Peptone.. .. .             | 37.675                                  | 34.700                        | 25.857                          |
| Albumose .. .. .           | 31.300                                  | 53.350                        | 15.964                          |
| Gelatine .. .. .           | none                                    | none                          | 9.826                           |
| Definite Compounds .. .. . | 5.525                                   | 5.930                         | 29.972                          |
| Mineral Salts .. .. .      | 8.285                                   | 1.025                         | 18.386                          |
| Water .. .. .              | 10.250                                  | 4.625                         | none                            |
| Insoluble .. .. .          | 9.965                                   | 3.980                         | none                            |

These figures mark profound differences of composition in the relative proportions of peptone and albumose. The peptone of meat albumen and the direct peptone of meat do not offer a constant ratio in regard to the proportional figures of albumose.

This anomaly may be imputed to the mode of preparation employed, which is more efficacious for the peptone of meat albumen than for that of coagulated albumen, which last is less easily peptonisable than albumen in solution in the preparation of meat peptone properly so called.

## THE ANALYST.

### A METHOD FOR THE DETECTION AND ESTIMATION OF PETROLEUM IN OIL OF TURPENTINE.

BY W. M. BURTON, CLEVELAND, OHIO.\*

THE use of the lighter boiling products of petroleum for the purpose of adulterating oil of turpentine is so well known to persons using these articles that little comment is necessary concerning the prevalence of this adulteration. Refined petroleum of the proper colour and gravity can be mixed with turpentine in such proportions as to elude the common methods of detection. The gravity, colour, and odour of the mixture can be made identical with that of turpentine; whereas paint made from such material is not durable, but is liable to crack and peel off soon after its application. The pecuniary advantage to the unscrupulous dealer is also a great temptation to perpetrate this adulteration on the large scale. The method which is here proposed is based upon the fact that petroleum is only slightly affected by fuming nitric acid in the cold, whereas turpentine is readily oxidised to various acids of the fatty and aromatic series, which are soluble in hot water. If, therefore, we treat a mixture of turpentine and refined petroleum with cold fuming nitric acid, the turpenes will all be converted into acids readily soluble in hot water, while the paraffins of the petroleum will remain almost entirely unaffected. These facts enable us to determine almost quantitatively the amount of petroleum contained in adulterated turpentine. The apparatus necessary for effecting this separation is very simple. A balloon flask of 750 c. cm. capacity is fitted with a two-hole cork stopper. Through one hole is inserted the tube of a glass stoppered drop funnel having a capacity of 100 c. cm. The flask is also connected with an inverted condenser. About 300 c. cm. fuming nitric acid of sp. gr. 1.4 are placed in the flask, and 100 c. cm. of the turpentine to be tested are measured into the drop-funnel. The flask is surrounded by cold water, and the turpentine is allowed to drop slowly into the nitric acid. As each drop strikes the acid, violent action takes place, with evolution of red fumes. It is well to shake the flask occasionally during the operation. When the turpentine has all passed into the flask, the apparatus is allowed to stand until all action is over. The contents of the flask are transferred to a large separating funnel and treated with successive portions of hot water. In this way all the products resulting from the action of the acid on the terpenes are removed, while any petroleum paraffins remain insoluble in water, and can readily be separated and measured.

Having procured some turpentine known to be free from petroleum, my assistant prepared mixtures of the pure turpentine with samples of refined petroleum of various boiling points. In order that my judgment in experimenting might not be influenced by knowing the quantities of material used, my assistant withheld from me the proportions employed in the mixtures. Ten mixtures were analysed, with the following results:—

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\* *School of Mines Quarterly.*

| Pure turpentine used. | Petroleum used. | Boiling point of petroleum. | Petroleum found by method described. |
|-----------------------|-----------------|-----------------------------|--------------------------------------|
| 66 c. cm.             | 35 c. cm.       | about 250°                  | 34·1 c. cm.                          |
| 80                    | 20              | 250                         | 18·9                                 |
| 70                    | 30              | 200                         | 29·                                  |
| 80                    | 20              | 200                         | 18·5                                 |
| 90                    | 10              | 200                         | 8·9                                  |
| 80                    | 20              | 100                         | 17·8                                 |
| 70                    | 30              | 100                         | 28·4                                 |
| 85                    | 15              | 100                         | 13·5                                 |
| 80                    | 20              | 75                          | 17·9                                 |
| 70                    | 30              | 75                          | 28·                                  |

It will be noticed that the sum of the amount of petroleum and turpentine used would be 100 c.cm. in each case, so that the number of cubic centimetres of petroleum found would also express the percentage of adulterant. It appears from the above results that the petroleum fractions, which boil at about 250° are least affected by the fuming nitric acid, while the low-boiling fractions are affected the most. But in order to keep the specific gravity of the turpentine where it should be, the higher boiling petroleum fractions must be used in the adulteration—a fact which is favourable for the application of this method in the analysis of such mixtures.

### A SIMPLE METHOD FOR ESTIMATING UREA.

By C. W. HEATON, F.I.C., F.C.S., AND S. A. VASEY, A.I.C., F.C.S.\*

SEVERAL years ago it was suggested to us by some of our former pupils that it would be convenient if a system could be devised by which urea could be estimated easily, rapidly, and accurately without specially constructed apparatus. The hypobromite method gives results which are quite correct enough for clinical purposes, and several forms of apparatus of great convenience and simplicity have been devised for its execution. The latest and perhaps the simplest is that of Doremus, recently advocated by Dr. Cruise, of Dublin.

There is no difficulty in using any of the instruments which have been recommended, and it is probable that physicians will prefer to employ some one of them when it is accessible. But such instruments are not always accessible, and are easily broken; and it is in any case desirable that the medical practitioner who chances to have no apparatus at his command except the ordinary weights and measures of pharmacy, shall be able, without trouble or loss of time, to make satisfactory estimations of urea. In the system arranged by us in 1884, and now for the first time described in print, absolute accuracy is not aimed at, but the maximum error of calculation is so minute as to be quite lost in the greater errors due to variations of temperature and pressure, and

\* *The Lancet*, May 10th, 1890.

to imperfect measurement which are incidental to any rapid process which depends on the measurement of the nitrogen and expelled by alkaline hypobromite. It is well known that this nitrogen amounts approximately to 92 per cent. of the total nitrogen of urea. The apparatus required is of the simplest character. In addition to the ordinary pharmaceutical measures, all that is really necessary is a thistle-headed acid funnel, about one foot of glass tubing, and a couple of bottles. It is well to assume that no other appliances are available. The reagents are bromine and caustic soda.

The following arrangements are made:—1. An eight-ounce bottle of any form is fitted with a thistle-funnel and bent glass delivery tube, as though for the preparation of hydrogen. The lower end of the funnel should be bent upwards, like a small hook, to prevent gas from passing up it. 2. A small basin or breakfast cup may be used as a pneumatic trough, a four-ounce, or larger, bottle of any form being filled with water and inverted in it in such a manner that the end of the gas delivery tube can readily be brought under the mouth of the bottle. 3. A 40 per cent. solution of good commercial caustic soda is prepared. For example, half a pound avoirdupois of soda may be dissolved in water and when cold diluted to one pint.

The analytical process is as follows:—1. Into the gas generator is poured by means of the funnel one fluid drachm of bromine washed in by ten fluid drachms of the soda solution. The generator may then be immersed in cold water, and the inverted bottle of water placed over the end of the delivery tube. 2. Two fluid drachms of urine, very carefully measured, are added and washed in by exactly one fluid drachm of water. The three fluid drachms so added will of course cause an equal volume of air to pass into the receiving bottle. This is allowed for in the appended table. The generator is gently shaken; brisk effervescence takes place, and gas equal in volume to the liberated nitrogen is collected in the receiver. The generator should be kept as nearly as possible at the temperature of the air. 3. When the evolution of gas ceases, the receiver is removed from the basin by means of the thumb or a glass plate and placed mouth upwards on the table. It is now only necessary to measure in minims the quantity of water required to fill it. After deducting 180 (which may be taken as 200) minims due to the air displaced by the urine, each 100 minims of water added represent 0.25 per cent. of urea in the urine examined. If the urine contains more than 3 per cent. of urea, it is best to dilute it with an equal volume of water before making the determination.

The following table gives the percentage of urea corresponding to the volume of gas liberated, as shown by the quantity of water required to fill the bottle:—

| Minims of<br>water required. |       | Percentage<br>of urea. | Minims of<br>water required. |       | Percentage<br>of urea. |
|------------------------------|-------|------------------------|------------------------------|-------|------------------------|
| 200                          | .. .. | 0.00                   | 900                          | .. .. | 1.75                   |
| 300                          | .. .. | 0.25                   | 1000                         | .. .. | 2.00                   |
| 400                          | .. .. | 0.50                   | 1100                         | .. .. | 2.25                   |
| 500                          | .. .. | 0.75                   | 1200                         | .. .. | 2.50                   |
| 600                          | .. .. | 1.00                   | 1300                         | .. .. | 2.75                   |
| 700                          | .. .. | 1.25                   | 1400                         | .. .. | 3.00                   |
| 800                          | .. .. | 1.50                   |                              |       |                        |



## DETECTION AND QUANTITATIVE ESTIMATION OF ORGANIC AND IN-ORGANIC POISONS IN BODIES.

By DR. ANTON SEYDA.

*(Continued from page 96.)*

## (c.) DETECTION AND ESTIMATION OF ARSENIC.

If no mercury or antimony are present, 50 or 100 c.c. of the liquid are put into a Marsh's apparatus and tested for arsenic. The zinc must be first put into hydrochloric acid for ten minutes, and then washed with water, in order to free it from traces of adhering arsenic. Of course before lighting the hydrogen or heating the reduction tube, one must wait until all air has been expelled. The fluid must be introduced in small quantities, otherwise there may be too much frothing. It is as well not to try and get arsenical spots, as these only form well when there is a rapid evolution of hydrogen and a large quantity of arsenic; but it is best to produce the arsenical mirrors, which may afterwards be sealed if necessary, and produced as evidence in court.

If the amount of arsenic was not too small, and one has succeeded in getting at least two mirrors, the tube is cut with a diamond in such a way as to get four pieces of the mirror. The following tests are then applied: One piece is heated and the arsenical odour observed. The second piece is moistened with sodium hypochlorite, when the mirror should of course disappear. The third piece is treated with nitric acid, and, after evaporating the acid, the residue is tested with silver nitrate for arsenious or arsenic acid. The fourth piece is heated with ammonium mono-sulphide, and the arsenic made into the yellow sulphide. These four tests are amply sufficient.

If arsenic has been found, it is quantitatively estimated as follows: The liquid is warmed and treated for twelve hours with hydrogen sulphide, then put aside in closed flask for about five days, until the precipitate has completely settled. After removing the excess of hydrogen sulphide by a current of carbonic acid, the precipitate is filtered off and washed. The filtrate, as a rule, gets turbid, but one need not pay much attention to this, as the cloudiness *may* be due to a trace of arsenic, but is generally caused by organic matter.

To purify the precipitate, it is best to use a solution of ammonium carbonate, which will leave at least the bulk of the free sulphur behind. After evaporating the solution, the residue must be treated with nitric acid, the solution evaporated and the product fused, best in a porcelain crucible, with a mixture of nitre and potassium—sodium carbonate. After dissolving the mass in water, it is best to slightly acidify with nitric acid, and after completely removing the carbonic acid and nitrous acids by boiling, once more to throw down with hydrogen sulphide. The precipitate must then again be made into arsenic acid,\* and the solution, after concentration, be precipitated with magnesia mixture. To make sure of its purity, it is as well to redissolve the precipitate after slight washing with dilute ammonia, in hydrochloric acid, and once more throw down with ammonia. I have adopted with great success the proposal of de Koninck,† who dissolves the arsenical precipitate of the filter by means of nitric acid, evaporates the solution, and gradually

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\* Note by translator. Very conveniently done with bromine water.

† See ANALYST, 1888, p. 178.

heats the residue to redness. The pyroarsenate may be kept, or if there is not much of it, may be made into mirrors of metallic arsenic by means of the Marsh's apparatus, in the way already described.

(d.) TESTS FOR OTHER METALS, TIN EXCEPTED.

If mercury, antimony, and arsenic are absent, the fluid is made alkaline with *pure* sodium hydrate, then acidified with acetic acid, and, after heated to boiling, treated with hydrogen sulphide until it is cold. Sodium carbonate is now added until alkaline reaction, and the corked flask set aside until the liquid has become quite clear. After collecting the precipitate (which, as a rule, consists mainly of ferrous sulphide) on a filter, it is washed with solution of sodium hydrogen sulphide until the washings run off colourless. The filtrate is kept for further investigation. The precipitate is now put into a porcelain dish, cautiously oxidised with nitric acid, and the acid evaporated off. The residue, after being moistened with a drop of strong soda, is mixed with a little dry sodium carbonate and put by degrees into a silver crucible containing fusing nitre. After cooling, the fused mass is exhausted with water, the alkaline fluid saturated with hydrochloric acid (in a beaker), and filtered off from traces of silver chloride through filter paper, but if permanganate should be present, through asbestos, the liquid is then qualitatively and, at the same time, quantitatively analysed by the usual methods.

About the metals, which are not precipitated by hydrogen sulphide from their acid solutions, I want to make some observations. As a rule, the separation of iron, zinc, and aluminium in presence of phosphates of lime and magnesia will have to be carried out. I proceed as follows: The hydrochloric solution of the sulphides is, after evaporation, mixed with some chlorine water and again concentrated. The residue is treated with slight excess of ammonia, which throws down the phosphates, the filtrate is acidified with acetic acid, heated to boiling, the zinc thrown down with hydrogen sulphide, and the zinc sulphide collected on a weighed filter. The phosphatic precipitate, which may contain alumina, is dissolved in nitric acid and heated in a platinum dish with metallic tin, which will cause the separation of the phosphoric acid as stannic phosphate. The filtrate is precipitated with ammonia, and the precipitate, after washing, burnt together with the filter. The ash is then fused with caustic soda for half an hour, which will form aluminate of soda, from which the pure alumina may be isolated in the usual way, after first extracting the alkaline mass with water, and filtering from any insoluble matter.

(e.) ESTIMATION OF TIN.

The sodium sulphide solution is acidified with hydrochloric acid boiled and treated with hydrogen sulphide. After twenty-four hours the precipitate is filtered off and washed with solution of ammonium acetate. The filter and contents is then heated in a porcelain crucible until the sulphide of tin has been converted into oxide, which oxidation may be assisted by the use of nitric acid. As, however, the oxide may contain traces of iron, it is best to fuse it in a silver crucible with pure caustic soda (free from water) for half an hour, at a temperature just high enough to melt the soda. After exhausting the mass with water, the fluid is filtered, acidified with hydrochloric acid and

the tin precipitated with hydrogen sulphide. The stannic sulphide is then converted into oxide and finally weighed.

#### FINAL REMARKS.

Among the normally occurring metals of the human body must be reckoned potassium, sodium, calcium, magnesium, iron, and manganese. But one is sure to find also, aluminium, copper, zinc; even tin and lead. Of the last four there is, however, seldom more than one centigram in a full-grown body. Traces of these metals of course get into the organism through the use of contaminated food, or impure beer, etc. If more than a trace is found inquiries should be made whether the deceased has been habitually taking medicines containing doses of, say, mercury or lead, or even, arsenic. As regards alumina (considering this is a constituent of sandy matter, clay, dust), traces of this substance may even get into the organs during the post-mortem examination, which, as we all know, is sometimes not too neatly conducted. As is well known, the organic matter rendered soluble by the treatment with chlorine is precipitated by hydrogen sulphide both in acid or alkaline solution. The removal of this organic matter by fusion with nitre answers very well for arsenic, antimony, and tin, but suppose there were mercury, this would volatilise. As I, however, test for mercury first by a special process, there is no danger of not finding it.

Contrary to the usual plan, I test for arsenic directly in the acid fluid, and only *then* proceed in the conventional way when the organs contain decided traces of free nitric acid, mercury, or aniline colours. Notwithstanding Otto's objections, I prefer this direct way of testing, which in fact had already been recommended by Marsh himself. It saves the troublesome treatment with hydrogen sulphide, which substance has lately become somewhat notorious as a possible source of arsenic.

To ascertain the influence of nitrates, I carried out the following experiment:—From a weak hydrochloric acid solution of .75 per cent. nitre and .33 per cent. arsenious acid, I added 1 c.c. to portions of organs, which were mixed up with water containing 5 grms. of potassium chlorate. After treating with acid as described, and freeing the filtrate completely from chlorine, the liquid was tested in the Marsh's apparatus, in which hydrogen was evolved from zinc and hydrochloric acid. After eight hours, practically all the arsenic had deposited in the reduction tubes. I must observe that addition of sugar seemed to favour the reaction.

From this experiment it seems that the presence of chlorides, and even nitrates, does not interfere with the formation of gaseous arsenic hydride, at least when there is plenty of zinc and acid, and sufficient time is allowed. Besides, as nitre speedily passes into the urine, no quantity of nitrate to speak of will ever be present in the organs when they are being tested for arsenic.

I further made a second experiment to ascertain the influence of free nitric acid. A small quantity of arsenical fluid was put into the Marsh's apparatus, and a mirror was soon obtained. When nitric acid was added, the generation of arsenic hydride seemed to cease, but it began to reappear after about twenty minutes, when no doubt all the nitric acid had been reduced.

Much has been said about the formation of solid arsenic hydride in presence of



## SILVER FROM COBALT.

The following are the results obtained :—

|   | Silver present<br>in grams. | Cobalt present. | KCN in grams.   | Total dilution. | Strength of<br>current in c.c.<br>O-H gas per<br>minute. | Time in hours. | Silver found. |
|---|-----------------------------|-----------------|-----------------|-----------------|--|----------------|---------------|
| 1 | 0·1788                      | 100 p. c.       | 4 $\frac{1}{2}$ | 200 c.c.        | 0·35 c.c.  | 16             | 0·1728        |
| 2 | "                           | "               | "               | "               | "  | "              | 0·1747        |
| 3 | "                           | "               | "               | "               | "  | "              | 0·1758        |
| 4 | "                           | "               | "               | "               | "  | "              | 0·1697        |

Recalling our experience in separating mercury from cobalt, we reduced the quantity of cyanide to three grams., and obtained :

|   | Silver present,<br>in grams. | Cobalt present. | KCN in grams. | Total dilution. | Current in c.c.<br>O-H gas per<br>minute. | Time in hours. | Silver found. | Difference in<br>per cent. |
|---|------------------------------|-----------------|---------------|-----------------|---|----------------|---------------|----------------------------|
| 5 | 0·1788                       | 100 p. c.       | 3             | 200 c.c.        | 0·35 c.c.                                 | 16             | 0·1794        | + 0·33 per ct.             |
| 6 | "                            | "               | "             | "               | "   | "              | 0·1782        | - 0·33 "                   |

From experiments made to learn the action of the current upon solutions of cobalt in the presence of a great excess of potassium cyanide, we know that the higher cyanide of cobalt—the cobalticyanide—is produced, and may it not be this which in some manner combines with the last traces of mercury and silver to form double cyanides not decomposable by the current strength employed in our experiments, which, if increased, would throw out not only the mercury and silver, but also some cobalt ?

With cadmium, the double compound, if formed, may be more readily broken up, hence the separation is easily made. By reducing the quantity of potassium cyanide with mercury and silver, we afford no opportunity for the production of cobalticyanide in such quantity as to appreciably affect the deposition of the other metals.

## COPPER FROM CADMIUM IN THE PRESENCE OF SULPHURIC ACID.

From the fact that it is possible to precipitate cadmium completely from the solution of its sulphate, containing free sulphuric acid (Smith, *American Chemical Journal*, 2, 42), and as copper is also deposited under similar conditions, the separation of these metals, when in this form, would hardly be expected. The experiments given below show that, notwithstanding all this, their separation can be effected under the conditions indicated. The first results were negative :

Ten c.c copper sulphate (0·1975 gram. metallic copper), 10 c.c. cadmium sulphate (0·1828 gram. metallic cadmium), 1 c.c.  $\text{H}_2\text{SO}_4$  (sp. gr. 1·09), with 150 c.c. water were

electrolysed with a current generating 0.4 c.c. O-H gas per minute. The copper was fully precipitated, and with it considerable cadmium.

In a second series of three experiments, similar to that above, excepting that the current only gave 0.22 c.c. O-H gas per minute, the copper was entirely precipitated, but carried down some cadmium with it.

In a third series of three experiments, the sulphuric acid in each dish was increased to 5 c.c. (sp. gr. 1.09). The current gave 0.22 c.c. O-H gas per minute. The copper was not completely precipitated, and cadmium had deposited on the copper.

The fourth series was made up as follows:—

(1) 10 c.c. copper sulphate = 0.1975 gram. copper.

10 c.c. cadmium sulphate = 0.1828 gram. cadmium.

10 c.c.  $\text{H}_2\text{SO}_4$  (sp. gr. 1.09).

100 c.c. water. Current = 0.3 c.c. O-H gas per minute. Time, 12 hours. The copper deposit weighed 0.1968 gram.

(2) Same as (1), copper found = 0.1964 gram.

(3) 10 c.c. cadmium sulphate = 0.1828 gram. cadmium, 5 c.c.  $\text{H}_2\text{SO}_4$  (sp. gr. 1.09).

100 c.c. water. Current as in (1) and (2). Cadmium was not precipitated.

In the fifth series of four experiments, a current generating 0.5 c.c. O-H gas per minute was employed. The quantity of acid was increased to 10 c.c. and 15 c.c. cadmium separated together with the copper.

The sixth series included five experiments:—

(1) 10 c.c. copper sulphate = 0.1975 gram. copper.

10 c.c. cadmium sulphate = 0.1828 gram. cadmium.

15 c.c.  $\text{H}_2\text{SO}_4$  (sp. gr. 1.09.)

100 c.c. water. Current = 2 c.c. O-H gas per minute.

Copper found = 0.1969 gram. copper.

(2) Same as (1), gave 0.1976 gram. copper.

(3) Same as (1) and (2), except that the current generated 0.3 c.c. O-H gas per minute. Copper found = 0.1975 gram.

Experiments (4) and (5) were like (3). The copper deposited equalled 0.1969 gram. and 0.1962 gram. Tabulating the results, we have:—

|   | Copper required. | Copper found. | Difference in per cent. |
|---|------------------|---------------|-------------------------|
| 1 | 0.1975           | 0.1968        | - 0.35                  |
| 2 | "                | 0.1964        | - 0.55                  |
| 3 | "                | 0.1969        | - 0.30                  |
| 4 | "                | 0.1976        | + 0.05                  |
| 5 | "                | 0.1975        | —                       |
| 6 | "                | 0.1969        | - 0.30                  |
| 7 | "                | 0.1962        | - 0.65                  |

The filtrates from the deposited copper were examined for that metal. (7) showed a trace of copper. Cadmium was not detected in the precipitated metal. Holding strictly to the conditions given above, will enable any one to effect the separation of these two metals in the presence of sulphuric acid.

University of Pennsylvania.

### ON THE EXPANSION OF FIXED OILS.

BY W. T. WENZELL, PH.M., M.D.\*

THE relations existing between given volumes of liquids and their temperatures do not appear to follow such simple laws as apply in the case of gases. Whilst it is well known that in general the rate of expansion in every liquid is in direct proportion as the temperature rises, that also liquids expand most rapidly whose boiling points are lowest, and that isomeric compounds such as ethyl formate and methyl acetate  $C_4H_8O_2$ , ethyl propionate and methyl butyrate  $C_5H_{10}O_2$ , etc., having the same boiling point, expand at the same or very nearly at the same ratio, yet, almost every liquid has a co-efficient of expansion different from that of any other liquid, and this co-efficient appears to vary to some extent with the changes of temperature; that is to say, that the rate of expansion is not uniform; a rule which holds good in all volatile liquids.

With the view of ascertaining whether fixed oils are governed by analogous laws, the writer concluded, inasmuch as he could not find data covering these, to investigate the subject. The methods usually followed for determining the cubical expansion of liquids may here be mentioned.

The actual expansion of any liquid may be ascertained by filling with it a small glass bottle whose cubical expansion is known, and weighing the bottle, with the quantity of liquid which fills it, at different temperatures. Another method which is more frequently used, and adopted by Pierre and Kopp in making their numerous determinations, is to observe the apparent expansion of the liquids in a so-called dilatometer, an instrument shaped like a common thermometer, and then correct these observations by taking into account the previously known cubical expansion of the glass.

It would be inaccurate to conclude that the expansion of a liquid between  $0^\circ$  and  $100^\circ$  amounted to one per cent. when the same quantity which filled 100 divisions at the former temperature occupied 101 divisions at the latter temperature, inasmuch as it is impossible to raise the temperature of a liquid without at the same time altering the capacity of the vessel in which it is contained. When a hollow vessel is heated its capacity increases exactly to the same extent as it would do if it was a solid mass of the same material and dimensions. Hence, we must consider the real or absolute expansion of liquids to be the apparent expansion, corrected for the simultaneous expansion of the vessel. These relations may be thus stated:—

The apparent expansion of a liquid is equal to the absolute expansion for the same interval of temperature diminished by the corresponding expansion of the containing vessel, and the co-efficient of absolute expansion in a vessel of any material is equal to the co-efficient of cubical expansion of the material of which the vessel is made. By

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\* Pharmaceutical Record.

the co-efficient of expansion is understood the increase in volume of the substance expressed in vulgar or decimal fractions for every degree of temperature. The mean cubical expansion of glass at temperatures of from  $0^{\circ}$  to  $100^{\circ}$  C. is  $\frac{1}{57034}$  or 0.00002663 for each degree; hence these fractions represent the co-efficients of expansion of this substance. Therefore, when once the cubical expansion of a vessel is known, the absolute expansion of any liquid can be easily deduced from its apparent expansion.

Six different samples of fixed oils were used in this investigation, three of which were of vegetable origin; the others were derived from the animal kingdom. For a dilatometer a glass flask of 510 c. cm. capacity was used, with a long neck graduated to one-tenth c. cm. at a temperature of  $62^{\circ}$  F. The flask was filled with the oil to O, and floated with the stem immersed in a double water bath, care being taken that the water bath and oils were exactly at  $62^{\circ}$  F., a temperature easily obtained in San Francisco without artificial aids. The whole apparatus was covered with felt and woollen envelopes, and every care taken to insure an even temperature. Through the top of the felt covering holes were cut to allow the stem of the flask and thermometer to be raised for inspection.

The heat was applied by a diminutive coal oil lamp, so regulated that an expansion of the oil not to exceed 1 c. cm. per hour was insured.

During the heating of the oils the flask was moved up and down about every five minutes, in order to heat the water surrounding it uniformly.

The following were the results obtained:—

*Olive Oil.*

| Dila-<br>tometer. | Ther-<br>mometer. | Differ-<br>ence. | Dila-<br>tometer. | Ther-<br>mometer. | Differ-<br>ence. |
|-------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 500 c. cm.        | $62^{\circ}$ F.   | —                | 506 c. cm.        | $92^{\circ}$ F.   | $5^{\circ}$      |
| 501 "             | $67^{\circ}$ "    | $5^{\circ}$      | 507 "             | $97^{\circ}$ "    | $5^{\circ}$      |
| 502 "             | $72^{\circ}$ "    | $5^{\circ}$      | 508 "             | $102^{\circ}$ "   | $5^{\circ}$      |
| 503 "             | $77^{\circ}$ "    | $5^{\circ}$      | 509 "             | $107^{\circ}$ "   | $5^{\circ}$      |
| 504 "             | $82^{\circ}$ "    | $5^{\circ}$      | 510 "             | $112^{\circ}$ "   | $5^{\circ}$      |
| 505 "             | $87^{\circ}$ "    | $5^{\circ}$      |                   |                   |                  |

*Mustard Seed Oil.*

| Dila-<br>tometer. | Ther-<br>mometer. | Differ-<br>ence. | Dila-<br>tometer. | Ther-<br>mometer. | Differ-<br>ence. |
|-------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 500 c. cm.        | $62^{\circ}$ F.   | —                | 506.1 c. cm.      | $98^{\circ}5$ F.  | $5^{\circ}$      |
| 501 "             | $67^{\circ}$ "    | $5^{\circ}$      | 506.6 "           | $95^{\circ}$ "    | $5^{\circ}$      |
| 502.1 "           | $72^{\circ}5$ "   | $5^{\circ}$      | 506.8 "           | $96^{\circ}$ "    | $5^{\circ}$      |
| 503.4 "           | $79^{\circ}$ "    | $5^{\circ}$      | 508 "             | $102^{\circ}$ "   | $5^{\circ}$      |
| 505.1 "           | $87^{\circ}5$ "   | $5^{\circ}$      | 509 "             | $107^{\circ}$ "   | $5^{\circ}$      |
| 505.7 "           | $90^{\circ}5$ "   | $5^{\circ}$      | 510 "             | $112^{\circ}$ "   | $5^{\circ}$      |

It will be seen that, although the above figures do not all give whole numbers, yet the expansion of mustard seed oil agrees with the olive oil, the expansion of each respectively being 1 c. cm. for every  $50^{\circ}$  F.:  $72.5^{\circ} - 62^{\circ} \div 2.1$  c. cm. = 5.

*Cotton Seed Oil.*

| Dila-<br>tometer. | Ther-<br>mometer. | Differ-<br>ence. | Dila-<br>tometer. | Ther-<br>mometer. | Differ-<br>ence. |
|-------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 500 c. cm.        | $62^{\circ}$ F.   | —                | 506 c. cm.        | $92^{\circ}$ F.   | $10^{\circ}$     |
| 502 "             | $72^{\circ}$ "    | $10^{\circ}$     | 508 "             | $102^{\circ}$ "   | $10^{\circ}$     |
| 504 "             | $82^{\circ}$ "    | $10^{\circ}$     | 510 "             | $112^{\circ}$ "   | $10^{\circ}$     |



| <i>Lard Oil.</i>      |              |             |
|-----------------------|--------------|-------------|
| Dilatometer.          | Thermometer. | Difference. |
| 500 c. cm.            | 62° F.       | —           |
| 510 „                 | 112° „       | 50°         |
| <i>Castor Oil.</i>    |              |             |
| Dilatometer.          | Thermometer. | Difference. |
| 500 c. cm.            | 62° F.       | —           |
| 510 „                 | 112° „       | 50°         |
| <i>Sperm Oil.</i>     |              |             |
| Dilatometer.          | Thermometer. | Difference. |
| 500 c. cm.            | 62° F.       | —           |
| 510 „                 | 113° „       | 50°         |
| <i>Cod Liver Oil.</i> |              |             |
| Dilatometer.          | Thermometer. | Difference. |
| 500 c. cm.            | 62° F.       | —           |
| 510 „                 | 112° „       | 50°         |

These experiments show that 500 c. cm. of either of these oils require 50° F. to expand 10 c. cm. or 5° F. to expand 1 c. cm. As the co-efficient of expansion is expressed in Centigrade degrees, therefore a reduction from Fahrenheit to Centigrade is necessary.

$$50^{\circ} - 32^{\circ} \div 9 \times 5 = 10^{\circ} \text{ C.}$$

Ten degrees C. increase 500 c. cm. of oil to 510 c. cm., which equals 1° C. to each c. cm. in the 500 c. cm., hence  $\frac{1}{500} = .0020000$  the apparent rate of expansion, and co-efficient of apparent expansion, .00200000  
 + Co-efficient of expansion of glass, .00002663  
 = Co-efficient of absolute cubical expansion of oils, 0.0202663

In conclusion, the author would direct attention to facts elicited by this paper, that, unlike all volatile oils and liquids, the fixed oils made the subject of this paper have the same co-efficient of expansion, and that their rate of expansion is uniform for all degrees of heat from 62° F. (16.6° C.) to 112° F. (44.4° C.)

## REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

**DETECTION OF YOLK OF EGG IN FOODS.** WICHELHAUS (*Pharm. Zeit.*, 1890).—Although phosphoric acid or its salts are insoluble in ether, this fluid is an excellent solvent for lecithin, a product of decomposition of vitellin, the albuminous body of the yolk. This lecithin, when saponified, yields a notable quantity of phosphoric acid, which may be estimated in the ordinary way after ignition of the soap. As the theoretical yield is 9.2 per cent. phosphoric anhydride the proportion of lecithin may be calculated by multiplying the phosphoric acid formed by 10.87. If not found in too minute quantity, an analyst may safely conclude the food contained yolk of egg.

L. DE K.

**ANALYSIS OF SODIUM ALUMINATE.** G. LUNGE (*Zeitschr. f. Angew. Chemie*, No. 8, 1890).—This compound is used in the manufacture of soap, and is an ingenious device for introducing excess of mineral matter (alumina). The analysis presents, of course, no difficulty when performed in the ordinary gravimetric way, which is, in fact, the only

good plan when there is any notable excess of silica. If, however, there is no danger of this being the case, the author proposes the following volumetric process, which is sufficiently accurate for technical purposes.

About 20 grams. of the compound are dissolved in a litre of water; 10 c.c. are mixed with phenol-phthalein and titrated whilst hot with normal hydrochloric acid. This gives the soda. Methylorange is now added and more acid slowly added until the fluid has become permanently reddish. This will give the alumina. It is as well to repeat the titration, adding the bulk of the acid at once, and then drop by drop. L. DE K.

ESTIMATION OF MINERAL OILS IN FATTY OILS. GRITNER (*Zeitschr. f. Angew. Chemie*, No. 9, 1890).—One of the most convenient processes is the one devised by Horn (see ANALYST, 1888, p. 184), which consists in saponifying the sample with alcoholic soda, and extracting the dry mass with chloroform. The author finds, however, that when the mineral oil preponderates the extraction becomes tedious, and he therefore proceeds as follows:—About 3 grams. of the sample are saponified in a porcelain dish with 20 c.c. of a solution of 25 grams. of caustic soda in a litre of spirits of wine. After the alcohol has evaporated the mass is mixed with sand and then put into a cartridge which is covered with a little filter. The extraction by means of chloroform is performed in the Soxhlet as usual. The chloroform is finally distilled off and the residual oil dried at 100° C.

If the chloroform is not pure it is best to redistil it over sulphuric acid. The sand used must be well washed with hydrochloric acid to free it from lime, otherwise there is danger of forming a lime soap, which is far from insoluble in chloroform. L. DE K.

NEW TEST FOR NITROGEN. E. DONATH (*Chem. Zeit.*, 1890).—About .05 gram. of the substance is boiled with a solution of 1 gram. potassic permanganate and 20 c.c. of saturated potash ley, adding more permanganate if required. After dilution with water, the excess of the permanganate is destroyed by adding a little rectified spirit, and the liquid filtered off from the precipitated manganic hydrate. As part of the nitrogen has been oxidised to nitrous acid, it is easy to get the test for this acid by the addition of hydrochloric acid, potassic iodide, and starch. Sometimes the oxidation proceeds further and a nitrate is formed, which may be shown by the brucine test.

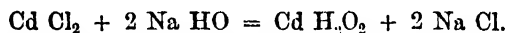
As the author succeeded in getting nitrous or nitric acid from pepsine, urea, quinine, coal, etc., he believes it to be a good general test.

This reaction will also explain why in the albumenoid ammonia process only a portion of the nitrogen is converted into ammonia. L. DE K.

VOLUMETRIC ESTIMATION OF CADMIUM IN PRESENCE OF ZINC. W. MINOR (*Chem. Zeit.*, No. 21).—The sample is dissolved in hydrochloric acid and filtered off from any lead. Besides cadmium and zinc, the liquid contains iron, and often traces of arsenic. The cadmium is now precipitated with hydrogen sulphide, and the cadmium sulphide collected and weighed. It, however, always contains more or less zinc, often as much as 5 per cent. It is, therefore, redissolved in hydrochloric acid, and after boiling, treated with sodium hydrate in excess, which throws down the cadmium and redissolves the

zinc. The amount of the latter (reckoned as sulphide) is then ascertained by titrating with standard solution of sodium sulphide, and deducted from the joint weight of cadmium and zinc sulphides.

An alternate process, suitable under some conditions, is based on the following principle: Neutral cadmium solutions are precipitated by sodium hydrate according to the equation



Therefore 1 c.c. normal soda = .0558 cadmium.

In applying this process, the solution must, of course, be free from excess of acid and any heavy metal. Therefore, in presence of zinc and iron, the last is first precipitated with ammonia, and the filtrate after being neutralised with hydrochloric acid, treated with caustic soda. After washing the cadmium hydrate, it must be dissolved in hydrochloric acid, and the excess of acid completely expelled by evaporation. The residue is then fit for titrating with soda. As indicator the author uses either red litmus paper until faint alkalinity is observed, or paper moistened with sodium sulphide until no more cadmium reaction is observed. The test analyses are satisfactory. L. DE K.

ESTIMATION OF TELLURIUM IN MINERALS. E. DONATH (*Zeitschr. f. angew. Chemie*, No. 7, 1890).—The usual plan is to throw down the metalloid with sulphurous acid, although the author preferred the fluid obtained by acting with zinc on a mixture of sodium bisulphite and hydrochloric acid. This process not working well in presence of bismuth and other metals of the fifth group, the author now prefers to reduce with pure glucose (free from calcium compounds).

About 4 grammes of the finely powdered ore are treated in a porcelain dish, with the usual precautions with small quantities of nitric acid. The excess of acid is then evaporated off, without, however, decomposing the nitrates of iron, bismuth, or copper, as otherwise the tellurium would pass into the *ic* state. After rubbing the dried mass with an agate pestle it is moistened with strong sodium hydrate, which will cause the mixture to get hot, whilst black copper oxide separates. After about half an hour some more solution of soda is added, the liquid is filtered off and now boiled for twenty minutes with glucose, which throws down the tellurium. This may now be collected on a weighed filter, or made into oxide ( $\text{Te O}_2$ ) as follows:—

The precipitate is rinsed off from the filter with a warm mixture of two volumes of nitric acid and one volume of water, containing also a few drops of sulphuric acid. The solution is evaporated and the residue ignited and weighed. The process is easy and sufficiently accurate for technical purposes. L. DE K.

#### REVIEWS, NOTES, ETC.

A HANDBOOK OF QUANTITATIVE ANALYSIS, by JOHN MILLS, OF THE NORMAL SCHOOL OF SCIENCE, AND BARKER NORTH, ASSOCIATE OF THE NORMAL SCHOOL OF SCIENCE, ILLUSTRATED.—London: Chapman and Hall, Limited, 1889.

THIS is a very well-written and complete little book for students preparing for any examination in ordinary quantitative analysis, and it is claimed to be sufficient for the Associateship of the Institute. Whether this be so or not, it forms a series of well-

arranged exercises for students commencing the subject. It would be somewhat in the nature of "breaking a butterfly" to indulge in a criticism from the point of view of a practical analytical chemist, otherwise we could indicate one or two points where the authors fall short of what would be the true practice to ensure absolute accuracy, and we cannot absolutely agree with the short summary of the conclusions to be drawn from the result of a water analysis. Still, on the whole, taking the book for what it is intended, it is a useful compilation, and given a practical teacher to point out where it is to be amplified and occasionally modified, it will be found very convenient for the use of students.

DETECTION OF GROUND NUT-SHELLS OR OLIVE STONES IN PEPPER.—In reply to a correspondent we give the following method which is employed in the Paris Municipal Laboratory by M. Girard :—

(1) *Preparation of the reagent.* This is a solution of dimethylparaphenylenediamine and sodium bisulphite and is made as follows :—10 grams. of the ordinary commercial dimethylaniline are mixed in a basin with 20 grams. of pure concentrated hydrochloric acid. To this mixture 100 grams. of crushed ice are added and 100 c.c. of a 7 per cent. solution of sodium nitrate is cautiously introduced, a little at a time with constant shaking, and the whole is set aside for half-an-hour for the reaction to become perfectly complete. 30 to 40 c.c. of hydrochloric acid are then introduced, together with 20 grams. of pure tin foil, and the reducing action so caused is allowed to continue for an hour, at the expiration of which sufficient granulated zinc is introduced to precipitate the tin. The liquid is then filtered and neutralised with solution of potassium carbonate, which is added until a permanent cloud forms, and acetic acid is carefully dropped in until the turbidity just appears. 10 grams. of concentrated solution of sodium bisulphite are then added, and the whole is finally made up to two litres with distilled water.

(2) *Application of the reagent.* 2 c.c. of the reagent are placed into a porcelain saucer and a good large pinch of the pepper is sprinkled into the liquid and allowed to stand for some minutes. Pure pepper either remains without change or is only tinted a very pale rose, while all the adulterating particles of olive stones or other sclerogenous tissue are coloured a bright carmine. If some water be now added the heavier red particles collect together at the bottom, and a fairly good quantitative idea can thus be obtained.

The indication thus observed may be farther confirmed by repeating the experiment with a solution of sulphate of thalline (·5 gram. in 100 c.c.), which colours the sclerogenous tissue bright orange.

PREPARED COCOA.—We have been requested by a correspondent to give some particulars on this subject, and we now intend to do so, although, of course, all the matter is really perfectly well known to the professional section of our readers, who are, therefore, warned to skip this paragraph, and not to grumble at our occasionally providing a little reading interesting to the general public. Cocoa is, in its natural state, highly stimulating, but at the same time a very rich and somewhat indigestible substance, con-

taining a large amount of a fat known as cacao butter. To prepare cocoa for table, it is necessary that the amount of this fat should be reduced. This is attained by using one of two methods, viz.: (1) The roasted and ground cocoa is mixed with starch and sugar so as to dilute its richness; (2) before grinding the cocoa, it is heated and pressed, whereby a considerable amount (generally nearly one-half) of its natural fat is squeezed out. This latter method is decidedly the more desirable one, because not only is the fat removed, but all the other nourishing and stimulating principles are at the same time concentrated. A typical cocoa of English manufacture by this process is found in the well-known Cadbury's cocoa essence. This article has always been, in our experience, exceedingly constant in its nature, and the last time we analysed it we found:

|                                    |     |                     |     |     |        |
|------------------------------------|-----|---------------------|-----|-----|--------|
| Fat                                | ... | ...                 | ... | ... | 28.12  |
| Theobromine                        | ... | ...                 | ... | ... | .95    |
| Natural starch, sugar, fibre, etc. |     |                     | ... | ... | 40.85  |
| Soluble albumenoids, 6.61          | }   | Total flesh formers |     |     | 21.34  |
| Insoluble albumenoids, 14.73       |     |                     |     |     |        |
| Natural mineral matter             | ... | ...                 | ... | ... | 4.94   |
| Moisture...                        | ... | ...                 | ..  | ... | 3.80   |
|                                    |     |                     |     |     | 100.00 |

Here then is what constitutes, in our opinion, a specimen of a properly-prepared cocoa, nothing added to dilute its flesh-forming or stimulating properties, and nothing deducted except the indigestible fat. There are, of course, other excellent prepared cocoas in the market, but we have purposely chosen Cadbury's as the type to illustrate these remarks because it is really the standard English article, and was, we believe, the first so manufactured. Indeed, until it was brought out, the only style of cocoas known to English consumers were compounds that produced, when cooked, what was practically little more than sweetened starch flavoured with real cocoa. Even now persons are to be found who prefer such articles, or who simply drink what their grocers send them and call it cocoa. If our correspondent happens to be one of these, let him try the real article, prepared by the fat extraction method, and give up buying extra starch and sugar under the name of prepared cocoa. To give a still more striking confirmation of our remarks let our readers glance at the following average amounts of flesh-forming ingredients present in the substances named:—

|   |     |     |     |     |       |
|---|-----|-----|-----|-----|-------|
| Natural cocoa                                   | ... | ... | ... | ... | 13.00 |
| Good wheaten flour                              | ... | ... | ... | ... | 14.00 |
| Cocoa prepared with added starch and sugar      | ... | ... | ... | ... | 6.00  |
| Cocoa prepared by extraction of fat (Cadbury's) | ... | ... | ... | ... | 21.00 |

EXALGIN may be distinguished by the following simple test from acetanilid and phenacetin: 1 gram. is dissolved in 2 c.c. chloroform (acetanilid requires 6 c.c. and phenacetin 20 c.c. chloroform) and 20 c.c. petroleum ether (sp. gr. 0.650) added; the solution should remain clear. 10 per cent. phenacetin and 20 per cent. acetanilid can be detected by the formation of a precipitate after standing a short time.—(E. Hirschsohn).

A TEST FOR HYDROGEN DIOXIDE.—The solution to be tested is made alkaline, and then a soluble neutral salt of lead or copper added; a deep brown-red precipitate, rapidly changing to red, and finally to white, indicates hydrogen peroxide. In concentrated solutions effervescence is also to be observed. Ozone solution (Lender's) does not give this test.—(A. O. Gawalowski).—*Am. Journ. Pharm.*

# THE ANALYST.

JULY, 1890.

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*Owing to the pressure of the Society's matter this issue of the ANALYST is entirely devoted to the same.*

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

An ordinary meeting was held at Burlington House on Wednesday, the 11th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

The following gentlemen were elected as members:—S. J. Steel, F.C.S., Blackheath, as Associate; T. H. Pearmain, Assistant to Mr. Allen.

The following gentlemen were proposed for election as members:—G. A. Milne, F.C.S., Analytical Chemist, Norton Malton; H. Barclay, Analytical Chemist, Workington; Edgar Richards, of the American Inland Revenue Department.

The following papers were read and discussed:—

“On Dyed Sugar.”—By C. E. CASSAL.

“On some Recent Advances in our Knowledge of the Sugar Group.”—By Dr. W. J. SYKES.

“On some Points in the Analysis of Milk.”—By H. DROOP RICHMOND.

“Notes on the Chemistry and Detection of certain Hop Substitutes.”—By A. H. ALLEN.

The country meeting of the Society will be held at Gloucester on the 25th inst. Full particulars will be duly announced.

## REMARKS ON THE BITTER OF HOPS AS DISTINGUISHED FROM THE BITTER OF QUASSIA AND OTHER “HOP SUBSTITUTES.”

BY MATHEW A. ADAMS.

*Read at Meeting, May, 1890.*

It was at the commencement of 1875 that a consideration of the bitter principle of the hop was first brought under my notice with a view to distinguish it by chemical or physical means from the bitter of quassia or other substitutes of a similar nature, reputed to be used in the composition of sundry proprietary articles variously called “Hop Substitutes,” “Hop Supplements,” “Bavarian Hop Bitter,” and so on, which articles

were extensively advertised, and said to be largely used to replace the true hop bitter in the brewing of beer.

The "Hop Growers' Association," as it was called, applied to me for advice and assistance in the endeavour to discover some means for distinguishing, by chemical analysis or otherwise, between these substances. Positively nothing appeared then to be known concerning these bitters, and being unable myself to supply any information, upon my advice, certain prominent chemists who had made the question of food analysis a special study were consulted, but without any satisfactory result.

In September, 1875, the Association offered a reward by advertisement in various professional papers of £100 for the discovery of a method for detecting the presence of quassia or other substitutes for hops in malt liquor. This offer, if I remember right, was to hold good for twelve months. Two others and myself were appointed to test and adjudicate upon the methods of any claimants for the reward, but no claim was made and not a scrap of information obtained. So the offer of a reward lapsed, and the whole proceeding was reckoned a failure.

Meantime I had been turning the thing over in my mind, and was invited to undertake the investigation myself, and a small sum was set apart as remuneration to me for doing so.

I was supplied with samples of the various hop substitutes then in the market. I obtained samples of various medicinal tonic bitters which appeared to enter into the composition of the hop substitutes, and worked at the thing myself with the result that, early in 1877 I was able to write to the Chairman of the Hop Growers' Association announcing my ability to detect foreign bitters in beer, and offering to subject myself to a trial. Twenty-seven samples were sent me to test my ability to do so, some of them had been specially prepared by the committee, and my analysis showed that nine had been bittered with foreign bitters and eighteen were not so bittered, and this was correct. The eighteen pure samples were mostly of porter from various parts of London. The Association were very much disappointed that quassia had not been discovered in any of these London beers, and they then proposed to undertake a roving expedition throughout England to find a beer with foreign bitter in it. I had no objection to that, but could not see the fun of doing all this work without being paid for it, and offered to disclose the secret of my process for the lapsed reward, or to do any number of analyses at a fixed fee. This they did not consent to, but put themselves into communication with some other chemist, but who that chemist was I never enquired and never knew. That was the end of my dealings with the Hop Growers' Association, and the subject of hop bitters, so far as I was concerned, was put altogether on one side, and no one, I imagine, will blame me for not being in a temper to publicly disclose the results of my researches for the benefit of a rival by whom I had been supplanted. In 1887, as you all know, Mr. Allen invited communication on this subject from members of this Society, and at the May meeting, which was well attended and wholly given up to a consideration of the matter, Mr. Allen read a very interesting paper on the subject, and many others, either by letters or voice, also contributed to the discussion that followed. The part that I took was to testify to the practicability of distinguishing between the hop and hop substitutes, which I did by private com-

munication with Mr. Allen before he read his paper, and also subsequently at the public meeting. In February, 1888, Mr. Allen again brought the subject forward for discussion, and I explained my method, so far as the use of sulphuric acid is concerned, and subsequent to this in a foot-note on page 46 of the ANALYST, Mr. Allen reports that he had succeeded with the sulphuric acid treatment on the sample of hops, which gave the sensible bitter extract (by the ordinary method of applying the lead test), and found all trace of bitter had disappeared, even when the concentrated solution was agitated with chloroform and the evaporated chloroform solution tasted.

It is not that I am over concerned to identify myself as the original investigator in the field that I have ventured to occupy a few minutes with this historical statement. My object is to repel an insinuation that I had unaccountably kept secret my knowledge on this subject. For the credit of our Society I take leave to say that there is no more liberal-minded body of men to be found than the members of this Society. I have never known an instance where information has been withheld for private interest or refused by one member to another when applied for. The value of this freemasonry among us is incalculable; but for this the public analysts of Great Britain could not have been the competent men they now are. Aye, nor would the present knowledge of food analysis be what it now is; and in passing I should like to say it has often occurred to me that the strongest argument to be found against the fusion of this Society with any other is the possible risk that to some extent the opportunity for this freedom of interchange of thought and experience within the limits of our special field might be jeopardised. Since the February meeting in 1888, the subject again fell into abeyance, and it was only a week or two ago that Mr. Robert Norton, the member for the Tonbridge division of Kent, called upon me to ask whether I could furnish any information on the chemical aspect of the question for the Select Commission of the House of Commons now enquiring into the causes of the depression in the hop industry. I consented to do so, and did give evidence on May 1st, and now ask your kind attention to a few hastily put together remarks on the subject.

Anyone by the unaided sense of taste may observe a wide difference between various bitters in the duration of their effect upon the palate, and this is a characteristic that seems to divide bitter substances, sharply, into two categories :—

1.—Fixed Bitters.

2.—Fugitive Bitters.

These characteristics manifest themselves

1.—Physiologically in their effect upon the body, and also—

2.—Chemically in their behaviour under chemical treatment.

A fixed bitter affects the organ of taste in a way that is enduring, and not only does the effect of the bitter last a long time, but also for the time being it appears to overwhelm the taste organs; so that these taste organs require a considerable time to recover their entire freedom to repeat their office. On the other hand a fugitive bitter has not anything like so penetrating an effect, and the effect lasts but a comparatively short time, leaving the palate clean and free to appreciate other flavours. Moreover, one can, as it were, taste through the bitter of the fugitive bitter, whereas the fixed



bitter covers everything, and, so to speak, monopolises the sense of taste, hangs about the mouth, and perverts other flavours for a long time.

In short, the stimulus to the gustatory fibres of the glossopharyngeal nerve, is in the one case transitory, but in the other long continuing, for which we shall, I think, presently find an explanation. The hop bitter will serve as an example of what I call a fugitive bitter and quassia of a fixed bitter. It is not only from a physiological, but in some respects also from a chemical point of view, that this characteristic distinction is displayed.

Quassia and its allies will stand a deal more rough usage, so to speak, and yet survive, whilst the hop bitter is destroyed; in a word the one is a much more stable compound than the other, but I take the liberty of applying the terms "fixed" and "fugitive" in a chemical sense, simply because by certain methods of chemical treatment, presently to be described, the fugitive is driven away whilst the fixed is left behind.

The proximate nature of the hop bitter is ascribed to several resins varying in intensity of bitter, but I hardly think its true nature has yet been positively and definitely made out. I suspect that a part, if not the whole, of this bitter is of the nature of a glucoside; at all events, this view fits in very well with the facts. For instance, fermentation removes a large part of the bitter, and *boiling a 2½ per cent. decoction of hop with 2½ per cent. of sulphuric acid under a reflux condenser for two or three hours every trace of bitter is entirely removed.* But quassia and its allies are not at all affected by this treatment. This is the key note of the distinction between the fixed and fugitive bitters—the latter being more or less of the nature of the glucosides, on this account disappearing by conversion into glucose in the acidified decoction, and in the mouth by digestion through the agency of the ferment proper to the saliva—and so we can now understand how it is that the palate when dealing with a fugitive bitter clears up so quickly, while, on the other hand, a fixed bitter, being insusceptible of fermentive change maintains its bitter effect so long.

As regards the argument that the fugitive character of the taste of hop bitter is due to its glucoside nature, allow me to draw your attention to the fact that salicin, a very bitter substance, but also a well-known glucoside, has this same fugitive characteristic in respect of taste, for when a saturated solution is placed on the tongue all bitterness soon vanishes.

The hop bitter, however, though it is of the nature of a glucoside, is by no means easy of conversion, so that prolonged boiling with the sulphuric acid is necessary, and fearing that this somewhat severe treatment might possibly, to a certain extent, attack some of the fixed bitters, it seems as well to take advantage of the selective power of the basic acetate of lead to assist and hasten the removal of the bitter, so that the process I employ is as follows:—

#### FIRST PROCESS.

The decoction is made to boil, and basic acid of lead solution is added until the point of saturation is just reached. The boiling is continued for some time, after which the precipitate is filtered off, and the filtrate at once treated with sulphuric acid until there is a decided excess. The lead sulphate is filtered off, and the clear acid

filtrate gently heated until by evaporation it is reduced to a small bulk. Chalk is then added to remove the acid, the decoction filtered, and if nothing but hop has been used in the decoction, all bitterness will have disappeared.

But if quassia or any of the hop substitutes has been used it will be as bitter as ever, and in proportion as it is concentrated more bitter; if it was a mixture of hop and quassia, the hop bitter will have been removed, leaving the quassia behind. I have spoken of quassia as an example, but the same holds good for Gentian, Chiretta Calumba, and a very large number of vegetable bitters, probably all of the fixed or unfermentable bitters, and certainly for all the various so-called hop substitutes that have come to my hands. There is, of course, no difficulty in applying these principles to the detection of the false bittering of beer, and to the best of my belief so long as we have to deal with new hops the process as described is always reliable.

I have said that the hop bitter is not easy of conversion; in some cases it is more stubborn than others. My original experiments were conducted upon samples of new hops only, but recently, a few days ago, I was experimenting upon some old hops—too old for use in brewing—and I was surprised to find that there was a certain amount of residual bitter left in the final filtrate at the end of the experiment, so the process was repeated with additional care, but the second result was, perhaps, more bitter than the first. Thinking that it was possible some of the precipitate might have been redissolved by excess of lead acetate, in a third experiment the lead precipitation was done in fractions, care being taken in the first and second precipitations to keep well within the point of saturation, and so prevent, as far as possible, re-solution by the lead acetate; and yet the result was bitter, even more bitter than in either of the two first experiments. From this it appeared that the more carefully we precipitated the more completely we laid bare residual bitter. A similar result occurring when we treated other samples of *old hops* there seemed little doubt but that the *age* of the hops had something to do with causing the difficulty. For the moment we were nonplussed, but by the following expedient the difficulty was overcome in a very satisfactory way.

#### SECOND PROCESS.

Starting with the decoction of this obstinate sample, we raised it to the boil, and added barium hydrate solution till an alkaline reaction was obtained. This threw down a rich chocolate brown precipitate, which was filtered off, and the bright, rosy red filtrate was made just acid with sulphuric acid heated and then filtered, and the filtrate evaporated to about a quarter of its original bulk; by this time most of the bitter was gone. Then the lead treatment was proceeded with as in the first process, and the result was quite satisfactory, and for all practical purposes bitterless; and so far as my experience with the process has gone, it has never failed to remove hop bitter even in the most obstinate of old hops that I have yet come across; at the same time it has no effect upon quassia.

So that by this improved process it would appear to be possible not only to determine the presence of a foreign bitter, but even to discriminate between a beer that has been bittered by old from another that has been bittered by new hops.

I cannot pretend to have given this new process an extensive trial. I have not had the time to do so, but seeing it has proved successful in cases where the first process had

failed, only by reason of the age of the hops used, I am greatly in hopes that it will be found effectual in all cases, but I need hardly say that it is my intention, as time permits, to apply the process to every variety of hop, both as regards age and source, and in the improbable event of failure on account of some undiscovered peculiarity in respect of a particular sample of hops due to age, source, or other reason, we can with confidence fall back upon the simple, if somewhat severe, method of boiling with sulphuric acid, so that in any case the difficulty is solved.

So much for the chemical aspect of the case. Let us pass to a consideration of the fixed and fugitive bitters from a health point of view. This, although essentially a medical question, can be treated in a popular common-sense way, and if we continue to take the hop and quassia as illustrative examples, it appears to me that there is sound common sense reason for making a clear distinction between the two in respect of their general effects upon the human body. Very little precise knowledge is available as to what becomes of quassia when taken into the system, but from what we know of its behaviour under chemical and fermentive treatment, we may be quite sure it is not easily changed, and in all probability, like quinine and strychnine suffers little or no decomposition in the body, but is excreted with the urine, and probably also with the fæces in an unaltered condition; that it is carried along the whole tract of the intestinal canal, a point of considerable importance, there can be no doubt; sufficient evidence of this is found in the effectual vermifuge action it exerts upon ascarides (worms that reside in the lowest part of the bowel), so that with quassia we have to do with a drug that is incapable of digestion, and in this respect one that behaves like quinine and strychnine, drugs that have a more profound effect upon the body than almost any with which we are acquainted. On the other hand there is little or nothing to show that the hop bitter can exist for any considerable length of time in the body without undergoing complete digestion, and being assimilated into the system and turned to account as food. Well, you may be disposed to say all this may be true of the ultimate results of these substances when introduced into the body, but is it not also true that both manifest tonic properties, improving the digestion and so forth? Undoubtedly that is so, but even in this respect it is obvious that their action is not identical. The hop exerts a tonic action that is temporary lasting only so long as it remains undigested, for as soon as by digestion it has been converted into food it ceases to be a tonic. On the other hand, the indigestible bitter of quassia from first to last keeps up its tonic stimulation. No doubt in certain morbid conditions of the body this may prove an advantage, but in the normal state of health the digestion does not require to be perpetually goaded to action.

The word tonic, as we are now employing it, implies a special kind of stimulus upon the functional activity of the alimentary tract, and we may be quite sure that intervals of non-stimulation, in other words rest, are just as necessary for that part as any other part of our anatomy. It may be all very proper and salutary to rouse the energy of appetite and digestion, but in health to maintain an unnatural stimulation, and so cause a continuous nervous tension in the parts affected, it appears to me, must be prejudicial; it is as though a bow were always kept strung. I have often pictured to myself the beneficial effect of a transient tonic such as we have in the fugitive bitter of the hop, by the parallel effect we observe after a plunge into the sea and out again;

reaction follows upon the sudden short stimulus, and the benefit is obvious. On the other hand, if the immersion be prolonged the bather is not benefited; exhaustion takes the place of reaction, the bow has been too long strung. It is wonderful what tolerant bodies we inhabit, but we may depend upon it the tendency of unnecessary and prolonged stimulation of the digestive organs by the habitual use of fixed bitters is more or less prejudicial.

Turning to another point, I can fancy some reluctant convert to these views might say, "Ah! but how about the soporific, drowsy effect of the hops? Is not that a set-off, or even more than a set-off, for the injury you impute to the fixed bitter?" Well, let us see. In the first place, upon what authority does the statement rest that hops have a soporific effect. I have looked through all the books on *materia medica* that are at this moment accessible to me, and I can find very little justification for the imputation that the hop is soporific at all; the fact is, from a therapeutical point of view, the hop occupies a very humble place, so much so that by some modern writers, as Ringer for instance, is not even mentioned. This is what Garrod says:—"Hops are tonic and stomachic and slightly narcotic; in the form of bitter beer, taken with meals, they form a useful aid to digestion in some cases of atonic dyspepsia. The volatile oil is probably the narcotic principle, and in the form of a pillow, hops have been found anodyne and narcotic."

And Negilgan says:—"Much difference of opinion exists as to the therapeutical properties of hops; they are generally stated to be narcotic, but from the experiments made with them on animals by Majendie and others it would appear that this effect is not manifest when they are given internally, no matter how large the dose."

And Periera says:—"The odorous emanations (vapour of the volatile oil) of hops possess narcotic properties; hence a pillow of these cones promotes sleep, as I have several times witnessed." "Moreover, we are told that stupor has occasionally been induced in persons who have remained for a considerable time in hop warehouses. The lupulinic grains are aromatic and tonic. They appear also to possess soothing, tranquilizing, and, in a slight degree, sedative and soporific properties. But the existence of any narcotic quality has been strongly denied by Dr. Bigsby, Majendie, and others." "I have tried it at different times," says Majendie, "both the lupuline (lupulinic grains) in substance and its different preparations, on animals, but I have never observed that it is a narcotic, although this property is one which is most strikingly displayed in experiments on animals."

As regards the reputation of the hop pillow, which has been handed down from book to book, it is very doubtful if there be much in it—for although I live in the midst of the chief hop-growing districts I never knew of its actually being put in practice—I quite believe that it is an old legend that gained more credence than it deserved owing to the anecdote that King George III., being a sufferer from faceache, derived comfort and got sleep by the use of a hop pillow that a loyal subject of Kent presented to him. Be this as it may, so far as medical experience goes, there is really nothing to countenance the idea that the hop, except in its volatile constituents, contains anything soporific, and in point of fact I do not believe the hop contributes to the finished beer, so far as the consumer is concerned, anything beyond a delicious aroma and an agreeable salutary bitter.

I can see nothing but fallacy in the argument that "*stock beer*" is more heady and intoxicating than a "*present use beer*," because the former contains a pound or two more hops per barrel. Depend upon it, the difference has nothing to do with the hops; they, as we all know, are introduced by the brewer to give the stock ale its keeping quality, and it is the keeping, the maturing, that gives the beer its "*drowsy influence*." It is very well known that the ageing of beer is attended and accomplished by further fermentative and other changes which take place in the cask, and the products of this cask fermentation, which are of a totally different character to those of the primary fermentation, the alcohols, æthers, etc., that are produced, although but little further attenuation takes place, immensely increase the intoxicating property of the beer. No doubt they are amylic or other heavy alcohols; indeed, practical brewers' chemists acknowledge this. One, for instance, says: "It is useless to disguise the fact that English beer contains fusel oil. If not, I ask why it is that lager beer is not intoxicating; it frequently contains more alcohol than mild ale;" and again he says, "English beer undoubtedly contains heavy alcohols, æthers, and fatty acids, to which it owes the properties (intoxicating) wanting in German beer."

On the other hand, we have not far to seek for the explanation of the immense improvement that has taken place as respects the less intoxicating effect of modern as compared with old-fashioned beer. From beginning to end, science has fairly revolutionised brewing. There is no need for me to remind you gentlemen of the intelligent control that is now maintained over the temperatures employed in the mashing, in the fermentation and attemperation, nor of the importance of the skillful care that is now bestowed upon the selection and proportioning of the malt and malt adjuncts, and the microscopic watchfulness over the yeast. These facts considered, it is no marvel that beer has improved; it is far more of a marvel that the brewers' chemists, to whom the whole of the credit is really due should be ready with self-denying modesty to conceal their own just merits in an unfair attempt to fasten upon the indispensable, unoffending hop the demerits of the old-fashioned beer.

Gentlemen, I hope I have not detained you too long. If you think so, I must plead as excuse what took place when I was before the Committee of the House of Commons on the hop question a few days ago. I was asked, "Should you have any objection to lay before the authorities at Somerset House the full results of all your experiments?" to which I replied, "I should, as a matter of course, occupying the position I do hold of President of the Society of Public Analysts, feel the greatest pleasure in communicating all I know upon this subject to the Council of the Society of Public Analysts, and it would come, as a matter of course to be general knowledge. I have no wish or desire to keep the matter secret."

Question.—"And assuming that it might be necessary to make still further experiments, do you think we might rely upon the help of the body of Public Analysts over whom you have the honour to preside? Do you think they would help you in carrying out further experiments?"

To which I replied: "I think the history of our society would show that all that has been done to advance the methods of analysis of food has almost entirely originated with our society, and there has never been, so far as I am acquainted with the matter,

the smallest indication of reticence on their part, in withholding anything like a new method, or new knowledge, which has come to the knowledge of the members individually. The utmost liberality has been shown in that respect; in fact I think we have not had justice done to us."

Gentlemen, this contribution is a first instalment towards the redemption of that pledge. We all know that for an enquiry of this kind, besides skill, time and patience are needed to bring it to a perfect issue, and we well know that all that is required to secure the needful patience and skill is to convince you that occasion has arisen that will justify us in the expenditure of the time necessary for the investigation, and I feel sure, in the name of the society, I may venture to say that if legislation is dependent upon a satisfactory test for the detection of bitters other than hops in beer, we may be trusted to supply both men and methods capable of a complete solution of the problem.

#### DISCUSSION.

DR. SYKES (who had temporarily taken the chair) said they would all agree with him that they had heard a very interesting paper, both from a physiological and chemical point of view, and he invited discussion.

MR. GORDON SALAMON said: They must all join in the opinion that the President had communicated a most interesting paper, one which he could not help thinking embodied the result of his cogitation over the cross-examination to which he was recently subjected before the Select Committee of the House of Commons. For poetic treatment the paper left nothing to be desired, but from a scientific standpoint he was bound to take grave exception to much that had been said.

Before discussing it from that point of view, he would, however, venture to suggest that the President had chosen a most inopportune moment for reading his paper. He disclaimed all personal feeling in stating his opinion that the President should have brought his process to the notice of the Society instead of giving it publicity for the first time to a Select Committee of the House of Commons; more especially as the Committee might be contemplating a recommendation of legislation upon the strength of that process, backed as it was by the President's position in respect of their Society. They had been told that it was only a fortnight since that he received an intimation from Mr. Norton that he would be wanted to give evidence before the Committee, but he could not think that such a statement relieved the President from the duty of first of all making the Society's journal the repository of his process. The President had developed his process fifteen years ago, but it was only now, when he had given his evidence in the name of the Society, and the inquiry relating to the science of the subject had closed, that he came to ask them for an opinion as to the merits of his process. He thought that the course taken was much to be deplored, because it was certain that if he had first of all submitted the question to them, the cross-examination would have been anticipated, and the President would never have given evidence which had resulted in unintentionally misleading the Committee. The President was questioned by Sir Henry Roscoe with a facility and ability which they all knew him to possess, with the result that the President had come there that evening to inform his brother analysts that he had now abandoned his process—one, be it remembered, which he had informed the Select Committee only a fortnight previously, would enable him to go into the witness-box and swear to the presence of hop substitutes, and would, moreover, permit of the enforcement of a penal statute. That statement and that opinion he had recanted. He had substituted another process (No. 2, as it was called); but he (Mr. Salamon) would

warn him not to accept it without careful examination. He considered it to be as full of error as the abandoned No. 1 process.

Not being able to speak as a medical man, he could not discuss at length the President's contention as to the nutritive qualities of hop extract and the irritating qualities of quassia; but he did not think the position taken up was quite supported by the authorities upon the subject. The President has quoted from the older school of *materia medica* men, and had entirely ignored their greatest living authority, Lauder Brunton. By reference to his well-known book, he would find quassia described as a pure bitter stomachic tonic, the action of which is not thoroughly understood, and he would also find hops relegated to the category of hypnotics. Lauder Brunton further said that the combination of hops with lettuce in the form of a supper, consisting chiefly of beer and salad, had sometimes a very marked soporific action.

To use the President's own expression, the key-note of his argument was that the bitter principle of the hop was a glucoside. Hence, in the decomposition of the glucoside, the glucose was available as a food. He hoped it would not go forth that the Society approved that statement; for it did not embody the views generally held. The President had suggested that his case must stand or fall by that assertion. In that event he did not think there would be much difficulty in making it fall. The authority of Dragendorff upon such questions would scarcely be denied, and he supported Isleib (see "Plant Analysis," p. 147) in his confirmation of the view that it was not a glucoside at all.

Next, with respect to the statement that basic acetate of lead precipitates the bitter principle of the hop, it is curious that Mr. Allen and the President should entertain such opposite views upon a question so vital to the process. In the June number of the *ANALYST*, 1887, Mr. Allen said in his paper upon the detection of hop substitutes: "Several writers on the subject state that on precipitating a beer with basic acetate of lead the hop bitter is precipitated, and hence, if the concentrated filtrate still have a bitter taste, the presence of some hop substitute is certain. This difference seemed to me so important that I have very carefully investigated it, and find it perfectly in accordance with the fact." If this statement were contrasted with that of the President when before the Select Committee, the discrepancy would at once become apparent. Sir Henry Roscoe asked: "Are you aware in what respect Mr. Allen's method differed from yours?" "Yes. I first of all boil the sample with basic acetate of lead. Then, of course, I filter off the precipitate of the lead with such bitters as go with the lead. Then I acidulate my filtrate to get rid of my lead with sulphuric acid. Then I concentrate it into a small body, *when the sulphuric acid has the effect of discharging the fugitive bitter still further.*" That must be taken as a confession on the part of the President that the bitter of the hop—the fugitive bitter—was not wholly precipitated by sub-acetate of lead. Other matters were, however, precipitated, which, according to the President's own statement, and according to his (Mr. Salamon's) own experiments, would render any legislative action based upon the President's process wholly abortive. The desire was to provide a method which would allow an analyst to swear to the presence of hop substitutes in the presence of hop extract. How could they say they had got such a process when according to the President's own admission, confirmed as it was by numerous experiments which he (Mr. Salamon) had made, chamomile would pass unchallenged? He begged leave to quote from the President's speech, recorded in the *ANALYST* for June, 1887. He said "he had worked on the question of hop substitutes some ten or twelve years ago, and he found no difficulty in distinguishing between the bitter of hop and the substitutes used for it. The method he found most useful was the precipitation by sub-acetate of lead, and there was no difficulty at all with the ordinary bitters, such as quassia, calumba, gentian, chiretta, and wormwood all remaining in solution, whilst the bitter of hop, *and*

also the bitter of the chamomile, which behaves like the hop, goes down and leaves the solution bitterless." But it must not be imagined that chamomile was the only substitute that could be used in defiance of legislation founded on the President's process. Among the bitter principles of chiretta, it had been ascertained (*Pharmacographia*, a History of Drugs, Fleckigür and Hanbury, p. 393) that ophelic acid occurs in the largest proportion, and that it produces an abundant yellow precipitate with basic acetate of lead. He would refer the President to a research by the late Dr. Griess upon the presence of cholin in hops (*Trans. Chem. Soc.*); he believed that cholin had been isolated in certain samples of beer, and he would ask the President whether it was not a bitter principle, and whether it was precipitated by basic acetate of lead. In such a case might not a wrongful conviction be obtained? But above all he would ask the President whether his experiments had covered the addition of caramel to hopped beer. It was well known that prepared caramel was used very generally in the manufacture of beer. Had the President isolated the bitter principle of caramel? He certainly could not regard it as a hop substitute, and was it, he asked, removed by treatment with basic acetate of lead. He (Mr. Salamon) had made experiments which showed him that it was not so removed, and further, it resisted the action of sulphuric acid. He suggested that the President had not made the experiment in question, and that with the important class of black beers containing added caramel, a wrongful conviction might be obtained every day according to the President's process. He (Mr. Salamon) did not believe that a satisfactory method would ever be obtained by using basic or neutral acetate of lead, with or without sulphuric acid. It would have to rest upon a different action altogether, and he submitted with confidence that he took up a legitimate position when he told the Select Committee that it was impossible by any known process to swear to the presence of added hop substitutes in beer in the presence of hop. He asked the meeting to confirm him in his view, and to state that the No. 2 process of the President would be less efficient than the No. 1, because the basic hydrate would precipitate all acid principles, many of which were bitter. A further weakness was apparent in the President's process. It was most important. The concentration of the beer after removal of the lead, and the continued boiling with sulphuric acid, might, and he thought would, result in the destruction of several of the bitter principles they were most anxious to detect. They found, for instance, that gentio-picrin was decomposed by dilute mineral acids into glucose and a neutral principle. What would be the result of a concentrated acid in such a case?

The President had apparently laboured under the misapprehension that the bitter principle of the hop was the same in every kind of hop. Any brewer would tell him this was not the case. Had he ever worked with foreign hops, notably with Californians? He asked the question because it seemed to be an offence to use foreign hops in Kent, where the President had his laboratory.

Next he came to the influence of brewing waters upon hop extract. It was well-known to those who had really studied the question that the bitter of the hop varied greatly with these conditions, and no process would be worthy of consideration which did not take this into account. He therefore asked the President whether he had experimented, as he, Mr. Salamon had done, with waters derived from different geological formations. For example, had he tried waters from the coal formation, the carboniferous limestone, the marls in the sandstone, the millstone grit, or the dolomite? He did not think he had, and in that case he was not justified in speaking with dogmatism as he had done before the Select Committee.

The attitude adopted by Mr. Allen in this matter certainly required comment, and he could not pass it by unnoticed. When Mr. Allen went before the Committee,



his attention was drawn to the fact that he had recanted his process published in the *ANALYST*. He admitted it was so, but said that notwithstanding he was prepared to give evidence on oath as to the presence or absence of hop substitutes in beer. On being pressed by Sir Henry Roscoe, he admitted that he had made no fresh experiments to support his changed views, and that he had only conceived them a couple of days before giving evidence.

It was essential that this process should be conducted upon half a pint of beer, otherwise it would not have conveniently brought itself within the scope of the Sale of Food and Drugs Act. Dragendorff required two litres; Mr. Allen, in his process, published in the *ANALYST* for June, 1887, required one litre, but in his evidence before the Committee he stated his ability to make the test upon half a pint. He, Mr. Salamon, challenged his ability in this direction. He had repeated Mr. Allen's experiments, and could not get the same results. With regard to the question of quantity of beer, he would call attention to the fact that the hop extract did not amount to 5 per cent. on the total solid matter in the beer, so that, in experimenting upon half a pint, there would not be more than 15 grains. Replace, say, half of this by hop substitutes, and there would not be more than about 7 grains of hop bitter and a considerably less quantity of the substitute to work upon. They must not lose sight of that question. But in the experiments which Dr. Bell made, and which he detailed to the select committee, he worked upon beer artificially bittered with quassia to the extent of six pounds to the barrel.

Mr. HERON said he had for some years past given a good deal of attention to the subject of hops and their constituents, with a view to devising a means whereby their real marketable value might be determined by chemical analysis; and, in doing so, the bitter substances contained in hops had, as a matter of course, come under his notice. Since Mr. Adams had given his evidence before the Hop Industry Committee at the House of Commons, he (Mr. Heron) had repeated many of his old experiments, as well as tried new ones, in order to test the accuracy of the process mentioned by Mr. Adams in his evidence, and he had come to the conclusion that it was perfectly impossible, with our present knowledge of the subject, to precipitate out of solution, or to remove by any known means, the whole of the bitter substances of the hops. He had tried Mr. Allen's process as well as that of Mr. Adams. He had also used barium hydrate, as Mr. Adams had recommended in what he called his No. 2 process; and, although working in the most careful manner, he found all those methods to be practically worthless. In these experiments he had not confined himself to one kind of hops only, but had tried old as well as new hops, and foreign as well as English; and, treating them as he would, he still found in the final result, the bitter taste of the hop persistent.

No doubt Mr. Adams was well aware of all the work which had been done on the constituents of hops, and, if so, would know that there were at least three bodies contained in hops, which possessed a most distinct and decidedly bitter taste; one of these might possibly be precipitated by lead acetate, but there was evidence that the other two were not, and apparently could not, be removed by any other reagent either.

With regard to the whole subject they were simply in this position now. They knew that hops contained several substances possessing bitter properties, and until a thorough and exhaustive examination of different varieties of hops, of all ages and from all countries where hops are grown, had been made, until those bitter substances contained in them had been separated, and until their exact behaviour to chemical reagents had been determined, no one could positively assert anything with regard to those bitter substances or lay down any rigid rules for their detection.

Mr. Heron was rather surprised that Mr. Adams should refer to such antiquated

authorities as Pereira and others in connection with the stupefying effects or otherwise of hop extracts. He for one preferred to consult the works of such men as Lauder Brunton, Stevenson, Griess, and Williamson, men who had gone into this question in a thoroughly scientific manner, and who had shown beyond a shadow of a doubt that a narcotic principle did exist in hops, and which possessed, when in a very concentrated form, properties similar to those of other well-known narcotics; but he considered there was hardly any occasion to go beyond one's own observation to prove this. Every one there would doubtless agree with him that new whiskey contained an appreciable amount of fusel oil and other of the higher alcohols, and that a glass or two of such whiskey would contain more of these higher alcohols (to which Mr. Adams ascribed the stupefying effects of beer) than probably a gallon of strong ale; but what was the result when people indulged in an immoderate quantity of either? Simply this, that where whiskey was indulged in to excess an exhilaration of spirits was produced, which, in the sister isle, had, in days gone by, led to many a faction fight and row; but the very opposite was the case with people drunken with beer, they became drowsy and stupid showing very little inclination for fighting or for anything else, and he considered it was, therefore, merely begging the question for Mr. Adams to say that the stupefying effects of beer when indulged in to excess came from the alcohol contained in it and not from the hops.

There was another matter he would like to refer to, namely, with regard to the action of various brewing waters upon hops. There was no doubt that some of the mineral constituents of such waters exerted a greater extractive influence than others, as he had found by actual experiment. Again, the malt used in brewing would play some part, according as it contained more or less lactic acid. All these points should be considered in conducting experiments upon hops and in the conclusions derived therefrom.

He regretted very much that a paper on such a subject had been read at such a time and under such circumstances. Mr. Allen had read a paper on a similar subject two years ago, and in it referred in unfavourable terms to the use of sulphuric acid in precipitating the excess of lead in the filtrate. Mr. Adams was there and took part in the discussion which followed. He had then an opportunity of referring to his own process, in which he had placed so much confidence, but he allowed the opportunity to pass, and he (Mr. Heron) would like to ask Mr. Adams why he did not then bring his process forward for the benefit of his brother analysts, instead of on the present occasion, at the eleventh hour, when the secret could no longer be kept.

Very careful and numerous experiments ought to be made and tested under all kinds of conditions, before any method upon which must hang such an enormous amount of responsibility, and upon the result of which a person could go into a court of justice and swear that such and such was the case, was made public.

Mr. HEHNER said that by raising side issues, as had been done by the two previous speakers, and suggesting that various kinds of brewing waters, or hops from different countries might yield different results, the main question would be hopelessly obscured. Of course these matters would ultimately have to be studied, but for the present they had to deal with the comparatively simple question: Is there a possibility of distinguishing between the bitters of the hop and of hop substitutes, and does the process proposed by Dr. Adams effect such a distinction, or does it not? They had on the one hand the definite statement of Dr. Adams, that it was capable of doing it, whilst on the other they had an equally emphatic denial. He could not help thinking that the gentlemen who were thus at variance could not have operated in precisely the same manner. Small differences of manipulation might be at the bottom of this issue of opinion, and he thought it would have been well if Mr. Salamon and Mr. Heron had first com-

municated with the author of the paper to make sure they approached the matter upon the same basis.

During the most able speech of Mr. Salamon he had received the impression, as if that gentleman had been more anxious to reach those outside that meeting who were interested on the question, than to discuss for the benefit of the members of the Society. Public analysts had no political interest in the hop question, but it behoved them, in view of the possibility that they might be shortly called upon to distinguish between hop beers and otherwise bittered beers, to attempt the solution of this difficult question.

He quite agreed with Mr. Salamon as to the magnitude of the difficulties to be overcome. The number of bitter substances which might possibly be used as hop substitutes was so great, and their chemical value so widely different, that there was no possibility of classifying them by a few simple reactions. Only a short time ago it was believed that the precipitation with lead acetate sharply separated hop from other bitters. This belief proving more or less erroneous, Dr. Adams had now introduced a further mode of distinction, namely, the treatment with acids.

As a rule, glucosides on treatment with acid, yielded sugar and a bitter substance, whilst indifferent, non-glucosidic bitters were little affected, but in some instances the products of decomposition of glucosides were not bitter; thus colocynthin gave colocyntheine which was perfectly tasteless. Whatever might be the chemical nature of the hop bitters, he was of opinion that Dr. Adams had given them the means, by the successive treatment with lead and with acids, of narrowing the question and of enabling them more nearly to classify the bitters. For this they should feel grateful, even if it turned out that these views by themselves were not sufficient to sharply distinguish hop from all other bitters.

DR. JOHNSTONE said that in a paper of his on this matter about eighteen months ago he mentioned about the washing of the hops.

MR. CASSAL said that specific information was required as to the steps taken to watch over the hops in the hop-ground. He regretted that such experiments as he had been able to make in reference to this matter had up to the present been very few, and he was bound to say that hitherto he had not succeeded in removing the "bitter" in the manner directed. He recollected speaking to the Chairman (Dr. Sykes) upon the question, and his (the Chairman's) suggestion that the hops might have been watered with a solution of quassia. It was very evident that something far more definite and reliable than what they were at present in possession of, was required. From the point of view of a public analyst, who might be called upon to subject himself to cross-examination in the witness-box, the matter was far from being in the position that it should be. He did not think, like his friend Mr. Heron, that it would be for all time impossible to detect the presence of hop substitutes in beer; but he was disposed to think that the position adopted by Mr. Salamon before the Committee was upon the whole justifiable; it was, at any rate, safe. The Sale of Food and Drugs Act in its passage through Parliament had been largely affected by persons interested in adulteration in some form. The Act was exceedingly and unnecessarily cumbrous, and compared very unfavourably with certain Continental laws. The reasons for this were perhaps not far to seek. There was no earthly reason why public analysts should be compelled to adapt their processes of beer analysis to the examination of such quantities as half-a-pint, except that the present cumbrous law made it necessary for Inspectors to ask for small quantities in order not to arouse the suspicions of vendors prior to a purchase. There was no valid reason why an Inspector should not have power to seize any reasonable quantity of beer or of any other article which might be required for the purpose of proper analysis. The whole system of sample-taking appeared to have been devised for the benefit of adulterators,

It appeared to him (Mr. Cassal) that a little too much had been made by some speakers of the harm that hops might do to a consumer as compared with other things. They were asked to believe that the brewer was using hop substitutes in order to provide the public with something that was better for them, and in the profoundest anxiety to serve his fellow man. Every one might not see it in that purely philanthropic light. If an infusion of malt and hops was generally recognised by the public as beer, and if they wanted it they had a right to get it—and to get it free from adulteration ; but it was first necessary that what was to be understood by beer should be clearly defined.

Owing to the lateness of the hour, Mr. ALLEN and Dr. ADAMS confined themselves to a few short remarks. These gentlemen have since furnished us with the following replies :—

Mr. ALLEN says :—It is a curious and interesting fact that Mr. Salamon and Mr. Heron have never come forward with any hint or suggestion, and have not attempted to help the Society in any manner, though they have been fertile in prognostications of failure on the part of those who are attempting to solve an admittedly difficult problem. It appears from the speeches of Mr. Salamon and Mr. Heron that these gentlemen have made many thousands of experiments on the detection of hop-substitutes, and Mr. Heron goes so far as to say that not only has no process been devised in the past, but that it is absolutely impossible that any process can be devised in the future by which hop-substitutes can be detected in beer. It is very curious that, after taking so much trouble, neither Mr. Salamon nor Mr. Heron has placed a single one of their experiments on record, or laid before public analysts their reasons for believing the problem to be insoluble. It was said that Mr. Adams' paper was inopportune, but such an opinion comes from Mr. Salamon with a very bad grace. Is the paper inopportune because it is now of practical interest ; or because it is exceedingly inconvenient to Mr. Salamon and his friends, now that Parliamentary Committee is sitting to consider whether the unacknowledged use of hop-substitutes shall be permitted ? Mr. Salamon says that the President should have read his paper *before* he gave his evidence ; but where was the opportunity ? There was no meeting of the Society in the previous month, and two months ago the question had not arisen. And how comes it that Mr. Salamon has done that for which he blames the President ? Mr. Salamon has taken the extraordinary course of going before the Committee, and in the absence of and without consultation with me has undertaken to interpret—or rather misinterpret—views held by me. Mr. Salamon has thought proper to criticise my position in the matter, but apparently has never taken the trouble to master what I have written on the subject.

The use of acetate of lead has been recommended by a number of chemists as capable of precipitating the hop bitters, while leaving all or nearly all probable substitutes in solution. Dragendorff was apparently the first to suggest it, and he gave an elaborate scheme for detecting the substitutes in the filtrate. As stated in my paper published in the ANALYST for June, 1887, the distinction is referred to in Vincent's "Chemistry Applied to the Arts and Manufactures," in Wynter Blyth's "Analysis of Food," and forms an essential part of Ender's method of detecting bitter substances in beer, so that there is a very general consensus of opinion as to the value of the method. Having all this evidence before me when making the experiments which formed the foundation of the paper already referred to, I contented myself with a limited number of experiments in confirmation of this hitherto unquestioned proposition. Experience has shown that I was too hasty in this, and that the lead process as described by me in the spring of 1887 is unsatisfactory as a sorting test in the case of particular samples of hops ; but in face of the unanimous dictum of previous

workers this could not possibly have been foreseen. Indeed, a few minutes before the meeting at which my paper was read, Mr. Adams informed me that precipitation by lead was also the principle of the method he had successfully employed for the same purpose. But as my paper clearly indicated, I never intended the treatment with lead acetate as anything but a clarifying and sorting process, which was to be followed by extraction of the bitter principles with chloroform and ether, and the application of other tests to the principles so extracted. I contend that if this be done any traces of hop bitter which escape precipitation by lead are perfectly distinguishable from other bitter principles, and hence I was justified in saying that I was prepared to swear to the presence of these substitutes in all or nearly all cases, although if applied in the manner originally described by me the lead process did not make so sharp a separation as I had supposed. Hence, I have by no means "recanted" my previous expression of opinion that it is perfectly feasible to distinguish hops from hop-substitutes, with perhaps one or two exceptions, and I am quite prepared to detect and identify quassia and several other hop-substitutes in a perfectly positive manner without relying on the lead process at all. But much of the value of the lead process undoubtedly depends on the way in which it is used, a fact which explains the conflicting experience respecting it. For instance, I have stated before the Society at a previous meeting that a particular sample of hops, the bitter of which was not wholly removed by the ordinary treatment with acetate of lead, gave a perfectly satisfactory result when the lead was removed by sulphuric acid instead of by sulphuretted hydrogen. Whether such a change in the manner of removing the lead would be successful in every case I am not prepared to say. Then Mr. Heron said that the President adopts a method of treatment which was "condemned" by me in my paper published in the ANALYST for June, 1887, and he explained that he referred to the use of sulphuric acid for removing lead. But what I actually did say was "I *prefer* sulphuretted hydrogen to sulphuric acid or a sulphate, as the lead sulphide seems to carry down a notable quantity of colouring matter." This "condemnation" was certainly of a very mild character.

Dr. James Bell, in his evidence before the Committee, stated that the weak point of the lead process was that the extractive matter of beer was apt to prevent the complete precipitation of the hop-bitter by lead, and that in the absence of that extractive matter the precipitation of the bitter was complete. In answer to a further question put to him at my instigation, Dr. Bell definitely stated that if the lead treatment were repeated upon an extract obtained by ether or chloroform in the manner indicated in my paper before the Society of Public Analysts, the remaining trace of hop-bitter was removed, and that in that manner it was possible to make a perfect separation of the bitter of the hop and the bitters of hop substitutes. So far Dr. Bell's evidence is positive. His evidence as to the detection of the substitutes is discounted, as is that of Mr. Bannister, because they used such a proportion of quassia and other hop substitutes as would render the beer quite undrinkably bitter. I have operated on what I think a better plan, which is to take a mild beer containing no bitter unremoveable by lead acetate, and to add to such beer sufficient of the hop substitute to render it agreeably bitter. When such beer is subjected to the lead or other sorting process, there is no mistaking the bitter taste of the hop-substitute. It can be recognised not simply on half a pint of the beer, but on a mere fraction of that amount; in fact, there is much truth in the suggestion of Mr. Hehner, that my attempts to improve the methods of detecting hop-substitutes have rendered the tasting process too delicate. The very fact that Mr. Heron and Mr. Salamon seem to doubt the possibility of getting a bitter extract from half a pint of beer shows that their experience is of a very peculiar kind. They

have only got to *try* the process *once* on a beer bittered with quassia or chiretta, and their tongues will proclaim conviction. Mr. Salamon quotes Hanbury and Flückiger's "Pharmacographia," as an authority for the statement that of the bitter principles of chiretta, ophelic acid, occurs in the largest proportion, and that it produces an abundant yellow precipitate with basic acetate of lead, and he adduces this fact in support of his suggestion that chiretta would escape detection by Mr. Adams' process. But Mr. Salamon omits to state that chiretta also contains chiratin, a principle which some observers consider the most characteristic constituent of the plant. Flückiger describes chiratin as "intensely bitter," and Kemp actually employs basic acetate of lead to precipitate other matters and obtain it in a purified condition. Anyone can be excused for not being acquainted with the chemistry of chiretta, unless, like Mr. Salamon, he undertakes to criticise the work of others, and then he should at least take care to describe their researches accurately.

Mr. Salamon correctly refers to Dragendorff as a very high authority on the isolation and identification of plant-products, though in doing so he apparently overlooks the fact that Dragendorff has published elaborate schemes for the separation and identification of bitter principles, based primarily on precipitation by lead, and the use of immiscible solvents. But Mr. Salamon should at least quote his authority correctly. It is not correct that Dragendorff ("Plant Analysis," p. 147) supports Isleib in the view that hop-bitter is not a glucoside. What Dragendorff states is that Isleib confirms the statement of some unnamed observer that hop-bitter is not a glucoside. Mr. Salamon should be more careful.

Again, Mr. Salamon correctly states that by boiling with dilute acids, gentipicrin is split up into glucose and a neutral principle, but he omits to state that this neutral principle is *bitter*! I believe no one but Mr. Salamon can have understood the President to propose operating so as to produce concentrated sulphuric acid.

I am certainly inclined to share the doubt as to the glucosidal character of the hop-bitter, but I consider that the question had no practical bearing on the point at issue. The point, so far as Mr. Adams' process is concerned, is whether it is possible by a treatment with acetate of lead, perhaps supplemented in some way, to remove the bitter principle of the hop, while leaving the bitter principles of the usual hop substitutes untouched. Mr. Adams says he can do that, with the exception of chamomile, and it is no use for Mr. Heron to come forward and say that it is impossible; unless he takes the ordinary course of laying the results of his experiments before the Society in detail, and describing exactly his method of operating, so that we may be able to trace the cause of his failure. It is not contended by me, and I do not suppose it is contended by Mr. Adams, that it would be possible to declare in *every* instance that a beer contained hop substitutes when such might be present. Mr. Adams admits, and stated long ago, that the bitter of chamomile behaves like that of the hop with acetate of lead, and I have no doubt that, should a law be passed making it illegal to use hop-substitutes without declaring the fact, chemists would be found who would use all their ingenuity to circumvent the Act by discovering other bitters which would escape detection by any process which might be devised. Of course we have always to take account of that kind of action. Milk and butter are adulterated in a scientific manner according to the directions of professional chemists, and we may be sure the same will be done with beer. But it is not necessary that public analysts should be able to affirm positively that a beer is unadulterated, as Mr. Salamon seems to assume. What is required is that public analysts shall be quite certain that they are not liable to condemn, on wrong grounds, a beer bittered solely by hops. Mr. Salamon suggests that choline is a bitter principle, occurring in hops and present in beer, not precipitated by lead, and liable to be mistaken

for a hop substitute. But what is the truth? In all the descriptions of choline I have been able to find, not one author, except Griess, refers to it as a *bitter* substance. Even in the very paper by Griess (*Jour. Chem. Soc.* XLVII., 298), quoted by Mr. Salamon, and with which he must, consequently, be well acquainted, choline is merely described as having a "caustic, *somewhat bitter* taste." Its characters preclude its extraction from aqueous liquids by ether or chloroform, and Griess could not obtain more than 0.02 per cent. from hops. At the rate of 6 lbs. of hops per barrel, this means 2 milligrams. of choline per pint of beer, and Mr. Salamon suggests that the presence of this proportion of a "*somewhat bitter*" substance, natural to hops, and not extracted by ether or chloroform, would invalidate the detection of hop-substitutes! But, above all, Mr. Salamon lays stress on the difficulty he fears would be caused by the presence of added caramel in black beers, and he gravely asks if the President's experiments have covered such additions. Does Mr. Salamon seriously suppose that any public analyst would be likely to condemn a black beer under such circumstances. The lead-sorting test was never intended to be applied rigidly in such a case. It should, however, be within Mr. Salamon's cognisance that the books describe the bitter constituents of caramel as precipitable by lead acetate and other metallic salts. And if Mr. Salamon will take the trouble to *try* the effect of adding basic acetate of lead to a solution of caramel, he will find that by far the larger part of the bitterness is precipitated, and if he will then extract the concentrated filtrate with chloroform, and repeat the whole treatment on the chloroform extract, he will find that every trace of bitterness has been got rid of. If he uses neutral lead acetate he will probably find the bitter to be wholly precipitated by the first treatment. Hence, Mr. Salamon need not fear the confusion of caramel with hop-substitutes.

Mr. Salamon states that every brewer is aware that the bitter principle of the hop varies with the district in which the hop is grown. That the amount of bitter principle and the flavour are liable to variation will be intelligible to all; but Mr. Salamon appears to suggest that the chemistry of the hop varies with the initial of the name of the county or country in which the plant is grown, and that if the hop has been grown on a sandy soil, acetate of lead will not be likely to produce the same effect on an infusion as if the plant has been grown on a cretaceous soil. The first impression produced on hearing such contentions is that they are ridiculous; but if Mr. Salamon puts them forward seriously, he should at least back them up by experiments, showing the influence of the nature of the soil on the character of the bitters in the hops grown thereon. Such a paper would be a valuable contribution to the literature of plant-chemistry, but until it is produced it is impossible to treat Mr. Salamon's contentions seriously.

Then, again, Mr. Heron came before them and said that water containing 15 grains per gallon of sulphate of sodium extracted more of the bitter principle of the hop than water free from that saline constituent, and he wished them to believe, not only that more of the bitter principle was extracted, but that it was different in character. Mr. Heron said that he had proved that it was different in character because it was not precipitated by acetate of lead; but, unfortunately, Mr. Heron had apparently failed in precipitating the bitter of any hops by acetate of lead, although many chemists had employed that reagent for the purpose.

Mr. Salamon says he has examined waters from various geological formations, and asserts that it is well known to those who have studied the question that the bitter of the hop varies materially according to the origin of the water. Does Mr. Salamon mean to say that it is well known and that he has proved that the geological formation from which the water used for infusing the hop is derived affects the power of

lead acetate to precipitate the bitter principles? If so, where is a record of this "well-known" experience to be found?

In conclusion, we must admit that the problem in question is undeniably a difficult one, but the inherent difficulties are enormously increased by the action of a certain section. Chemists seem to be divided into two classes; those who never communicate any of the knowledge they possess, and are never to be found helping their brother chemists, though they are always ready to throw cold water on their efforts; and another party who feel it their duty to help their brother chemists by laying before them such information as they have, and who, perhaps, sometimes err, as I myself have done, by too much readiness in that way. In my opinion, the Society are very much indebted to the President for the paper he communicated. I do not suggest that we are in a position to rely on the modified method proposed, even as a sorting test, without due trial of it ourselves under various conditions. It is our duty to investigate the bearings of every process submitted to us, but the Society are indebted to any member who will bring before them his experience on any subject, so that it may be duly tested and verified by each member interested in the kind of work in question. But if we are to wait until we have examined samples of hops from every county in England, and every country in the world, grown on every kind of soil, and brewed with water from every geological formation, as Mr. Salamon suggests we ought to do, legislation on the question must be deferred till the Greek Kalends.

Mr. ADAMS says.—I should like to say the following in answer to some of Mr. Salamon's remarks:—

In the first place, my evidence before the Select Committee was not "given in the name of the Society," but on my own individual responsibility, and I had no alternative but to take the very first opportunity for placing my views before the Society, because I had pledged myself to do so. Moreover; so far as the Select Committee is concerned, the inquiry relating to the science of the subject "is not closed," but, on the contrary, has been specially kept open to afford an opportunity for me to make known my views in detail, so that they might be put to the test. As for misleading the Committee, or recanting my opinions, that is all nonsense. The most that can with truth be said is that my opinions have developed, and the House of Commons' Committee well know how prompt my action was to acquaint them with the discovery which I made and was the first to announce, viz., that there is a difference in the behaviour between new and old hops under chemical treatment. I devised a method (No. 1 Process) successful for distinguishing between the bitter of new hops and the bitter of quassia and its allies. Also another (No. 2 process), equally successful for the same purpose in the case of old hops. If I had not taken the course that I have taken as regards making known these things, I should have laid myself open to much blame.

Mr. Salamon says I have suggested that my case must stand or fall upon the assertion that the bitter principle of the hop is a glucoside. Such is not my suggestion, and I have asserted nothing of the kind. The suggestion is Mr. Salamon's, not mine. My assertion is that the facts fit in very well with the suspicion that a part, or the whole, of the bitter of hop is of the nature of a glucoside, and I beg to refer Mr. Salamon to the recent researches of Greshoff (*Allge. Brauer u Hopfen Zeit.*), which have proved my suspicion correct, by showing that a portion is a glucoside.

Mr. Salamon has confused two distinct and independent things—the facts and the explanation. The facts are facts; the proposed explanation is a theory. The validity of the process stands by the facts; the explanation must take its chance, and stand or fall with the theory. As respects Mr. Salamon's contention that because chamomile would escape detection by this process therefore the process must be abandoned, was there ever



an argument more ridiculous? It is quite unreasonable to expect any one single test to shut out every possible resource for adulteration. Experience of the working of the Food and Drugs Act is all against such an absurd contention. Objection might just as well be made to a process for detecting cotton-seed oil in butter because it was not fitted for the detection of beef stearin. For all practical purposes quassia is *the* thing that is used as a hop substitute. Chamomile was tried in 1882, but found quite unsuitable because of the large amount of volatile oil it contains.

Regarding the complaints of Mr. Salamon, and also Mr. Heron, that I had only quoted from the older school of *materia medica* men, thereby implying that I had not referred to any modern authorities, that is not true. Quotations were given from four sources, two of which, Pereira and Neligan, were among the greatest authorities of the past generation, and Garrod and Ringer are living authorities of the highest rank in the present generation.

Mr. Salamon had been pleased to designate Lauder Brunton as the greatest living authority. I will not stop to question his right of doing so; but I will only say that if such be really the case, more is the pity that Mr. Salamon should have given incomplete and therefore incorrect and misleading quotations from Brunton's writings. "By reference to his well-known book," Mr. Salamon must have observed when speaking of quassia he says, "In small doses it increases the appetite; in large doses it acts as an irritant, and causes vomiting." Again, to understand properly the passage relating to the supper of hops and lettuce, the context must be read, which runs as follows:—"Lettuce certainly seems to have a hypnotic action, but how much it depends upon the juice and how much upon the mechanical effect of the indigestible fibre of the lettuce upon the stomach in drawing blood to it, it would be hard to say. Hops are said to be hypnotic *in their combination with lettuce*. In the form of a supper, consisting chiefly of beer and salad, it has sometimes a very marked soporific action." So that, to produce the soporific effect, besides the hop this famous supper requires the *alcohol* of the beer, *the juice and also the indigestible fibres of the lettuce*.

And to show how utterly sceptical Dr. Lauder Brunton is of the soporific properties of the hop, see what he says in the very next following paragraph:—"A hop pillow is sometimes used in sleeplessness of fever, but its use is probably due not to the action of the volatile principles of the hop" (the only part to which soporific properties are usually attributed), "but to the mechanical elasticity and softness of the pillow."

Surely Mr. Salamon is to blame for want of candour giving us these quotations in full, seeing that they are necessary for the object he expresses himself so anxious, viz., that there shall be "*no unintentional misleading*."

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS. ON DYED SUGAR.

By CHARLES E. CASSAL.

(*Read at Meeting, July, 1890.*)

My attention has recently been directed to dyed sugar in consequence of a number of samples of moist sugar purchased in the ordinary way by the inspectors of one of the districts for which I am public analyst having been submitted to me. I am desirous of bringing the matter before the Society in its relation to the official work of public analysts, and of calling special attention to it as being one which appears to me to be of considerable importance, affecting general public interests as well as those of a large trade. Some two or three years ago it became known to many of us, and to persons in the trade, that certain firms had introduced sugar-crystals which had been artificially coloured. If I am correctly informed, it was not at first known in the trade that most, if not all, the sugar that was so introduced was beet sugar and not cane sugar; and I believe I am right in stating that the original name given to these products was that of *yellow cane crystals*. The present recognised trade name is "yellow crystals," and I do not suppose it will be denied, that the greater portion of the yellow crystals of commerce consist of artificially-coloured beet sugar.

The different samples submitted to me officially were plainly not the products of the same process of treatment, and therefore probably not of the same firm. They consisted of sugar-crystals possessed of various shades of golden-yellow, approximating in some cases to orange. Since examining these samples I have obtained authentic specimens

of the dyed sugars of different firms, and have been engaged for some time in experimenting upon them. Somewhat varying degrees of skill would seem to be employed in the preparation of the sugars. Some samples have been very skilfully coloured, while with others the work has been coarsely and roughly done. It will be found by examination with a lens that in the products of certain firms a number of crystals are entirely colourless and can easily be picked out, while with others the uniformity of colouring is far more perfect. In addition, large nodules of a bright orange colour are frequently to be found in what, I presume, may be called the more inferior products.

The particular sugar to which my attention was first directed was one the dye on which can be detected with the greatest ease. The sugar itself, or a solution in water, strikes a peculiar purple-pink colour on the addition of a few drops of concentrated hydrochloric acid. The colour is characteristic, and, if the dye is present in unusually small amount, is best seen when about 25 to 30 grammes of the sugar are just moistened with hydrochloric acid in a deep conical porcelain dish. On standing, the mixture becomes of a dark, reddish-brown colour. Acetic acid has a hardly-perceptible effect, but appears to slightly intensify the orange colour of the crystals. Sulphuric acid produces the same effect as hydrochloric acid, but the subsequent changes of colour are not properly perceptible owing to the charring that takes place. Although from the point of view of the public analyst it is a matter of little or no immediate importance to be able to detect the particular dye-stuff or dye-stuffs which have been used, so long as an artificial dye can be certified to be present, I may direct your attention to the fact that these reactions are very similar to those obtained with certain of the so-called Tropæolins, especially in some respects with those which seem to be known in commerce as "Tropæolin OOO" or "Orange I.," and "Tropæolin OO" or "Orange IV." Tropæolin OOO is the only one which I have examined which gives the rapid change of colour from purple-pink to dark-reddish brown when treated with hydrochloric acid; which change, as previously stated, was obtained with the samples of sugar now referred to. I have not, however, succeeded in satisfactorily dyeing colourless sugar-crystals with this substance by itself, the colour obtained being dissimilar from that upon the commercial sugar. Further, acetic acid, when added to solutions of Orange I. and Orange IV., does not produce any red or pink colour, but merely what appears to be an intensification of the orange colour. For these and other reasons, which I propose to communicate later, I considered that while the particular sugars referred to had probably been dyed with Tropæolins, it was likely that a mixture of these bodies had been used. I have now reason to believe, from information which has been afforded me, that this is what in reality had been done. It must be remembered that great confusion exists with respect to the application of these commercial names. My remarks here apply to substances which have been purchased in the ordinary way under these names.

Other dye-stuffs are, however, used for the purpose of colouring sugar-crystals, which do not give the reactions with hydrochloric acid, and it has therefore been necessary to devise means for showing their presence with sufficient reliability to admit of their being certified to. By applying the following simple process, I believe that any of the dyed sugars at present on the market can be sharply distinguished from those sugars which contain no colouring-matter foreign to sugar. About 100 grammes in most cases (less can

be used if absolutely necessary), of the sample is washed in a flask with alcohol of 90° per cent.. This removes the dye in the majority of the cases which have come under my observation. In some cases several washings are necessary, in others one only. Treatment with alcohol of this strength removes the whole of the dye, leaving perfectly colourless crystals. I have found that it is advisable to use weaker alcohol with some dyed sugars, viz., from 75 per cent. to 80 per cent. The solution is filtered from the sugars, evaporated to dryness, again taken up with alcohol, and a skein of silk or wool (preferably slightly mordanted with aluminium acetate) treated with the solution, warmed for some time in the water bath, and subsequently well washed with water. The skeins are permanently dyed of a more or less marked yellow colour if a dye has been extracted by the alcohol from the sugar.

A sample containing only such colouring-matter as is natural to sugar, even by repeated washings with alcohol of 90 per cent., does not leave absolutely colourless crystals, and does not give a solution capable of permanently dyeing silk or wool.

One of the substances which has evidently been very largely used for the dyeing of sugar is the so-called phosphine or chrysaniline. Sugar dyed with phosphine can at once be detected by the foregoing process. As commercial phosphine is usually the nitrate or the hydrochloride of chrysaniline, no doubt it is one of these bodies that is used. Fibres dyed with phosphine are turned to a very characteristic pale greenish yellow by alkalis which is more intense than the colour on the fibres when the latter is slight, and acids slightly redden them. When the amount of the dye upon the fibres is slight, the application of alkali serves to "bring out" the colour. I have obtained these reactions in every case upon fibres dyed with solutions obtained from sugar suspected of being dyed with phosphine. Fibres dyed with extracts containing the colouring-matter which, for the sake of convenience, I will call the "Tropæolin dye," are reddened by mineral acids.

It is evident that great quantities of dyed sugar are sold in London and elsewhere. It is very generally sold as Demerara sugar, and not as "yellow crystals." Out of fifteen samples of sugar purchased recently in one of my districts as "Demerara," eleven were unquestionably dyed, and the adulteration was detected easily in each case by the processes previously described.

I may be allowed to quote here an extract from a report which I made upon the subject a short time back. "Purchasers are under the impression that they are being supplied with genuine cane sugar (such as "Demerara"), whereas they are in reality getting sugar crystals which have been artificially dyed. In this way beet-root sugar can be coloured and sold as "Demerara," and it is generally admitted that weight for weight, under ordinary conditions of use, beet-root sugar does not give the same "sweetening" as cane sugar. A natural product having been tampered with by admixture with an artificial dye, whatever the real object may have been in the preparation of these sugars, it is obvious that the proceeding enables one article to be substituted for another." I am reliably informed that when "Demerara" is asked for on the market, cane sugar from Demerara is expected. The market price further, is stated to be from 17s. to 18s. per cwt. for Demerara, and for "yellow crystals" from 12s. to 13s. per cwt. A somewhat remarkable statement has been made with reference to my intention of certifying

artificially dyed sugar sold as Demerara as adulterated; namely, that cane sugar produced in the West Indies is dyed there with the same substances as those previously alluded to. This is merely an attempt to create a new definition for Demerara sugar. It might almost as logically be urged that if growers of coffee were to take to mixing chicory with their product before exportation, we should no longer be able to regard chicory in coffee as an adulterant. If the case is not strictly parallel the device is the same. It may, on the other hand, justifiably be contended that the sugars dyed as I have described are adulterated, for they can be certified to have been produced by dyeing colourless sugar crystals yellow, with an artificial organic colouring matter not natural to sugar.

Another aspect of the subject in reference to which I may again quote from my report is this: "Many substances used as dyes, and closely related to the classes to which those found belong, are known to be of a poisonous nature, while the action of others, when ingested, is unknown, while others again are asserted upon very insufficient and unsatisfactory evidence to be non-poisonous. Apart, therefore, from other considerations, these cases afford an illustration of the impropriety of tampering in such a way with articles of food without, at least, an open statement of what has been done. Although in dyeing an article of food the weight of the dye-stuff used must be exceedingly small as compared with the weight of the substance dyed, it must be admitted that the proper course of action in the present state of knowledge on the subject, is, as far as possible, to prevent the use of dye-stuffs of the general character indicated for colouring articles of food, if for no other reason, in view of probable and perhaps dangerous abuse."

In giving official certificates in these cases it will be tolerably obvious that it is undesirable, as well as unnecessary, to make too specific statements as to the precise nature of the dye or dyes that may have been used. The statements that may be made by experts in giving evidence in matters of this kind very largely depend upon the standpoint from which they are viewed. If, for instance, a definite statement were made as to the precise character of a complicated dye-stuff present in very small quantity in sugar, or anything else, it would no doubt be perfectly easy and conscientiously justifiable for the gentleman who had prepared the mixture to swear in the witness-box that the compound certified was not present at all, if the compounds were not in every respect, physical as well as chemical, in composition, as well as in constitution, identically the same in the opinion of every chemist of repute, or even of non-repute. Whatever the standpoint of the chemist consulted by the manufacturer may be, and I fully admit the propriety and value of such consultation, when professionally legitimate and publicly useful, the position of the public analyst is clearly defined. It is his duty to the community which he is appointed to serve to advise them of the existence of adulteration when it comes before him, and to do so without fear and without favour. That the dyeing of sugar in the manner indicated, and its sale as genuine natural sugar, and the application of the process for the purpose of enabling one thing to be palmed off for another, are adulterations, and, therefore, offences against the law, I, for one, have not the faintest doubt. The public have every right to expect that natural food products shall not be coloured with artificial dyes without an open statement of the fact. I desire to express my thanks to my assistant, Mr. Gerrans, A.I.C., for the help which he has afforded me in carrying out the necessary experiments.

## DISCUSSION.

DR. DUPRE said he had repeatedly had sugars submitted to him artificially coloured, but never as public analyst, and he should feel doubtful himself as to certifying sugar as adulterated, simply because it was artificially coloured, unless it was proved that the colouration was for the purpose of deceiving and enabling it to be sold as Demerara sugar. He would like to hear the opinions of other analysts as to whether the mere fact of sugar being coloured was to be taken as an adulteration. Butter was often coloured, so was milk, but many analysts do not consider the colouration of butter to be an adulteration. It had been a long-continued custom, and the public liked to see their butter yellow. If an artificial butter was coloured with a view to its being passed off as a genuine butter that was a different matter, but the mere fact of its being coloured was not an adulteration.

He quite agreed with Mr. Cassal that a public analyst was not bound to state the exact composition and character of what he supposed to be the adulterant, for if it came to that, and they should have to put the exact composition of such and such a substance, and if they linked together wrongly the oxygen and hydrogen, and were then liable to have their certificates set aside, the sooner they gave up the better. All that the public analyst could be expected to do was to say that this particular sample, say of sugar, is artificially coloured. If he can go a step farther and say that the colouring matter is so and so, that would be an advantage, but otherwise it would be a most dangerous thing for the public analyst to bind himself down to a particular composition. He did not think that the Act at all required the public analyst to do that.

He would like to ask whether Mr. Cassal had submitted these colouring matters to spectroscopic examination, because so many of them could be identified with a tolerable degree of certainty by means of the spectroscope.

He had also found that artificial colouring matter added to sugar was almost as easily distinguished by the action of water, natural sugars colouring water very slightly only, whereas artificially-coloured sugars imparted a marked colour, like chicory compared to coffee.

The colouring matter added might be the same kind as that of the natural sugar, but there was this striking difference—when water was added to the sugar the artificial colouring matter was dissolved off readily and left colourless crystals, the natural sugar remained the same colour.

MR. A. W. STOKES said that the public analysts were on the horns of a dilemma. It is well-known that almost all Demerara sugars contain about one-third of a grain of chloride of tin per lb., while most other sugars were artificially coloured with aniline colours in minute quantities. So that, from Mr. Cassal's view of the subject, few moist sugars would pass as unadulterated.

Mr. Stokes gave the opinion of Mr. F. J. Scard, the analyst at Demerara of the Colonial Company, who contends that the sale of fictitious "Demerara sugar" should be stopped under the Merchandise Marks Act. Mr. Scard holds that Demerara sugar keeps at the head of the market because of its retaining the natural aroma, tint, and flavour of the sugar-cane. Over-refining gets rid of these, and produces a less palatable article. He contends that chloride of tin is used merely as a mordant to fix these natural qualities; its use could be dispensed with, though not at present conveniently.

MR. ALLEN said he thought they ought to distinguish between their present position and the position they might be in in the future. Dr. Dupré had raised the question how far they could obtain convictions under the Sale of Food and Drugs Acts in cases of mere colouring, provided that the colouring matter was harmless; but Mr. Cassal and the speaker had in recent papers foreshadowed the time when the present

law might be amended; and the more instances they could bring before the notice of the authorities, and the more facts they had to go on, the stronger would be their position whenever the time came for fresh legislation. It was, of course, very desirable where possible to positively identify the nature of the colouring matter used, but that was by no means a necessity, any more than it was necessary for them to specify the exact nature of the fatty matters added to butter, or than it would be to specify the exact nature of hop substitutes supposing that any legislation were to be founded on the investigation of the recent committee. Mr. Allen said he certainly objected to have anything put into sugar for the sake of colouring it and making it pass as Demerara sugar. It was possible that such an addition might be dealt with under the Trades' Marks Act, but it appeared to him that the two facts taken together, namely, that it was not Demerara sugar, and that the colouring was put in for the purpose of deceiving, would make a good case to go before a magistrate.

MR. B. E. R. NEWLANDS said it would be a very extraordinary thing to find a sample of sugar that was not coloured. All sugars, such as loaf, granulated, crystals, and yellow crystals were coloured by artificial means, either with a blue or yellow colouring agent, and if the vendors of one kind of sugar were to be punished for introducing a harmless colouring matter, then those of all other kinds of sugar would be equally liable to prosecution.

In the West Indies yellow crystals were produced by the action of sulphuric acid or of stannous chloride, or, as at home, by the addition of a colouring matter. In the former cases, two or three gallons of the agent were added to a panful of sugar, and what Mr. Cassal would call a natural colour was produced. A good deal had been said as to palming off refined yellow crystals as Demerara, but if they referred to to-day's papers, they would find that, in many cases, the price of Demerara was lower than that of yellow crystals, the former selling at from 15s. to 16s. and the latter from 16s. 3d. to 17s. 3d. per cwt. It is, therefore, evident that the latter realise a higher price than the sugars they are supposed to imitate.

In Mauritius, Demerara, and the West Indian Islands, sugar, in addition to being coloured by sulphuric acid or stannous chloride, was coloured in exactly the same way as by refiners in this country, and therefore it would be impossible by any process of analysis to decide as to its place of origin.

What useful object could be attained by prosecuting grocers for selling yellow sugar, beyond providing work for the analyst? They might as well prosecute people for selling coloured sugar candy or Chelsea buns, or anything else coloured by artificial dyes. Dr. Dupré had suggested that the presence of artificial colouring matter in a sample of sugar might be ascertained by washing it with water. It was, however, extremely difficult to find a sample of sugar from which the colour could not be removed by water; he had been promised such a sample as a curiosity, but it had not yet arrived.

In turning out a standard article, such as yellow crystals, it was necessary to keep the colour perfectly uniform, and the refiner, therefore, had to add a minute amount of colouring matter, not exceeding one part in fifty thousand, for this purpose.

Manufacturers of sugar in the West Indies had often occasion to colour their products in the same way, and the sample of so-called "genuine Demerara sugar" handed round by Mr. Cassal, was thus artificially coloured. Whilst defending the sale of yellow crystals, he of course agreed that it was highly improper to describe them as "Demerara" unless they were actually produced in that colony.

MR. IEHNER said, that inasmuch as several aniline colours were of a decidedly poisonous nature, it could not be denied that the public analyst had the right and the duty to concern himself with the question of dyed sugar, and that he should know the

exact nature of the colouring matters employed. He had no grounds for believing that injurious colours were used in this particular case, but just as a public analyst might not to know all details of technical and manufactory processes, so manufacturing chemists might possibly be ignorant of the physiological action of the colours which they added to food materials. As instances, Mr. Hehner mentioned Dinitro cresol (also known as Victoria yellow and under other names) and Dinironaphthol (Martins yellow) which were both eminently poisonous.

MR. HERON said he might say at once with regard to what Mr. Hehner said, that no colouring matters were used for colouring sugars which were of a poisonous nature; concerning the point brought forward by Mr. Stokes as to the use of chloride of tin in the West Indian plantations, such was not the case. As a matter of fact the chloride of tin was used there for the purpose of destroying the dark colouring matter present in the crudely prepared raw sugar and imparting to it a bright golden yellow colour so characteristic of Demerara sugar, and thereby making an inferior class of sugar appear of a better quality than it really was, and, as proof of his statement, he would ask any gentleman present, who was at all interested in this matter, to make a complete analysis of any West Indian sugar and compare it with an analysis of a home-refined sugar sold on the market as yellow crystal, and it would readily be seen that the latter was the purer of the two. He maintained that the colouring matter referred to by Mr. Cassal was not added to the sugar by refiners to give it a fictitious value, but merely to meet the public taste, which at present seemed to run in that direction, that this colouring matter was perfectly harmless to human beings and animals, and that the sugar sold as yellow crystal was in his opinion much purer and better in every way than any foreign sugar of a similar character at present on the market.

DR. DUPRE said that they as a scientific body should not accept the assertion of anyone, whoever he might be let sugar manufacturers assert ever so much that the colouring matter they added was innocent—he should not pay the slightest regard to it unless they were prepared to state the nature of the colouring matter added, and then let him judge whether or not it was injurious to health. Did Mr. Newlands really mean to assert that all their sugar was artificially coloured? He was under the impression that some years ago the —what they call natural —colouring matter of sugar was a kind of caramel, and he should be exceeding astonished if Mr. Newlands told them that our old-fashioned sugar-candy was coloured with chloride of tin or sulphuric acid.

That colouring was what he called natural which remained in the sugar when treated with water. Mr. Newlands said there was no sugar now in the market the colour of which could not be washed out by water; that was to say that no sugar manufacturers really gave them unadulterated sugar.

MR. B. NEWLANDS said that the lower qualities of sugar-candy did contain the natural colouring matters of sugar, viz., caramel and dirt. The better qualities were produced from raw sugar which had been coloured by the agency of sulphuric acid, stannous chloride, etc.

MR. HEHNER said he would desire to protest against the often exploded doctrine that we should in any way be guided by the popular wish in food matters. The popular wish had been used by sophisticators for many years past as an excuse for every abomination perpetrated upon an ignorant public; no kind of adulteration was ever carried out without its being alleged to be in obedience to the popular wish. Years ago pickles and preserved peas were sold as green as the leaves on the tree, coloured with copper, and bloater-paste made red with brick dust; nowadays mustard and cocoa was mixed with flour and starch—all mixed by the obeying manufacturer to meet the popular wish. The public analyst, however, had to disregard the popular wish and raise the standard of



purity of food, if necessary, *against* the popular wish. Was not even milk mixed with water because the people desired to have milk cheaper than it could possibly be produced by legitimate means? He hoped that public analysts would not allow themselves to be carried away by such phrases as "the popular wish."

MR. CASSAL, in reply, said he was very strongly of opinion that a public analyst was not bound to state the exact nature of an adulterant. He would go further, and say that it was always undesirable to enter into technical details of any kind before magistrates and others, who were utterly innocent of any scientific training, and therefore quite incapable of judging of the merits of the most elementary scientific questions.

Replying to Dr. Dupré, he stated that he had not as yet applied the spectroscope to attempt to identify the colouring matters, but that he proposed to do so. He desired to express his thanks as a public analyst to Mr. Newlands and to Mr. Heron for the opinions they had expressed and the admissions they had made. He was sure that the members of the Society generally would join with him in doing this, more especially those who occupied official positions as public analysts. At the same time he could not congratulate them upon the defence which they had endeavoured to make of the practice of colouring sugar with artificial dyes. He noted, with much satisfaction, that they did not agree with each other as fully as might have been expected, and that certain of the remarks which they had made were surprisingly contradictory. With reference to chloride of tin, for instance, the Society had been informed that it was used as a "mordant" to "fix" the "natural aroma, tint, and flavour of the sugar-cane," then that it was applied for the purpose of producing colour in colourless crystals; and, finally, "as a matter of fact," that it was used for destroying the dark colouring-matter of raw sugar. These statements appeared to require some revision by those who were interested in sugar manufacture, and he would leave the matter in their hands. It led him, however, to point out the necessity of distinguishing between sugars artificially coloured by producing a "natural" colour in the form of caramel, with such agents as chloride of tin or sulphuric acid, and dyeing with aniline dyes for a purpose which in all probability was very different. Mr. Newlands had told them that all sugars were coloured, and had referred to the use of blue for loaf sugar. It was hardly necessary to point out that this was an altogether different thing—it did not serve the purposes of deception. They had also been told about the prices, and he (Mr. Cassal) had been duly rated for meddling with a question which ought to be left to the superior ability of the "sugar expert," but he had also had the opportunity of consulting authorities even as great, perhaps, as those present, and the opinions they expressed were different upon both points.

It having been freely admitted that the dyed crystals were beet-root sugar, and that hardly anything else could be obtained on the market, he was glad to find Mr. Newlands agreeing with him that to sell "yellow crystals" as "Demerara" (which word implied *cane-sugar*) was highly improper unless they had been produced in that colony. In other words, beet-sugar should not be sold as cane-sugar, and anything which facilitated such a sale was therefore condemnable. In this connection he would remind members that of fifteen samples of sugar recently purchased as "Demerara" in Kensington, eleven consisted of dyed crystals.

What was the object of dyeing colourless sugar-crystals with an aniline dye or dyes? Mr. Newlands and his friends would not go so far as to deny that the dyes used were aniline derivatives of some kind. It was said that it was for the purpose of maintaining continuity of trade and of pleasing the public taste.

There was possibly some validity about the trade continuity argument, and he should be happy if he could bring himself to think that this was indeed the reason.

Butter and milk had been mentioned, and perhaps the continuity argument might apply in a limited sense to butter; he could not admit it for milk, and in reference to all food-products, colouring practices required to be sharply looked after. The object of most of them, if not all, was to produce a false impression on the mind of the customer; and, as had been pointed out, they were fraught with danger. The only satisfactory method was to treat the matter rigidly, and to make it compulsory upon all vendors of food containing extraneous products to state what they had done. The "public taste" excuse for adulteration had been fully dealt with by Mr. Hehner; it was a very ancient excuse, and nothing more need be said about it.

They had been told that all the colours used, or likely to be used, were absolutely harmless in any amount. That was a somewhat bold statement, and he (Mr. Cassal) fully agreed with what Dr. Dupré had said about it. Something more was wanted than the mere statement of a particular person or firm that what they in their wisdom chose to put into food was "perfectly harmless" on the strength of some nebulous experiments made by somebody—they knew not whom—somewhere.

The samples moistened with acid which he had passed round were intended, as he had said, to show the difference between a sugar which would give the peculiar pink colour with hydrochloric acid, and one which would not. He thought that he had made it sufficiently plain in his paper that he relied upon the removal of the dyes by suitable solvents, and their purification if necessary; and not simply upon the incident that some of these dyes could be detected at once by the addition of a mineral acid.

The attempt alluded to in the paper to prevent the maintenance of the definition which could at present be given to Demerara sugar by stating that cane-sugar produced in Demerara was there coloured with aniline dyes and then exported was certainly ingenious, and reflected great credit upon whoever had evolved the idea; but it was singular that those who believed in this theory should admit that nearly all, if not all, the dyed sugar on the market was beet. Even if it was admitted that dyes were applied to cane-sugar in Demerara, he contended that the case was not affected. It was simply adulteration in Demerara instead of in England. By Demerara sugar was understood cane-sugar, and cane-sugar containing only such colouring matter as was natural to sugar.

He thought that the Merchandise Marks Act could certainly be applied to the case, and if it were so applied some of the vendors of "crystals" or "Demerara" might be disagreeably surprised. The penalties were not likely to be of the trumpery kind to which they were accustomed under the present Adulteration Acts. He was much gratified to find that the general consensus of opinion in the meeting was in favour of the views which he had put forward.

*(Conclusion of the Society's Proceedings.)*

## METHODS AND APPARATUS IN USE AT THE LABORATORY OF THE BOURSE DE COMMERCE AT PARIS FOR THE ANALYSIS OF CERTAIN COMMERCIAL ORGANIC PRODUCTS.

By DR. MUTER.

*(Continued from page 89.)*

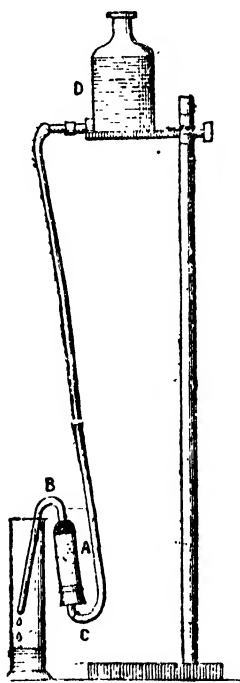
THE process adopted for the valuation of all sorts of tanning materials is the well-known one which consists in ascertaining the amount of absorption taking place from a solution of the tanning material when brought into contact with prepared hide or with Seimand's ossein, the result being reported under the name of "available tannin." The arrangements for simplifying the process and rendering it sufficiently rapid to admit of its being done at the small commercial fees charged at the laboratory are (like most of M. Jean's

arrangements) ingenious and effective. Before describing them in detail, it will be interesting to state that, disagreeing with the usual method of taking the specific gravity of the liquid before and after the maceration with the hide, M. Jean, for good and sufficient reasons, which he explained to us, considers it to be necessary to take the actual residue left on evaporation. The following is a short description of the process as actually in daily use :—

1. *Extraction of the Crude Material and Preparation of the Solution for Analysis.*—The bark is ground in the mill, or dry extracts are pounded in the mortar, so that a powder is obtained which will pass through an ordinary “25” sieve. The quantity to be taken for analysis is, of oak bark, 25 to 30 grams.; of stronger things (such as chestnut wood), 20 to 25 grams.; while, of very rich extracts, it may only be needful to weigh 10 or 15 grams. The quantity to be weighed is always to be judged by remembering that the solution, when actually made up to 250 c.c., must contain as nearly as possible 1 per cent. of “assimilable tannin.” The sample having been weighed, is now extracted by continuous percolation in a special apparatus. This consists of a cone of wire-gauze, which is tinned or nickel-plated, and into which the weighed quantity of the sample is put. This gauze receptacle is then introduced into an outer tube, connected to an upright condenser, and to the foot of the tube is attached, by means of a cork, a flask of 150 c.c. capacity, having 100 c.c. of water placed therein. The water in the flask being boiled, continuous extraction takes place, which entirely exhausts any material within the space of one hour. In the Paris Laboratory, where a large number of samples are

being constantly dealt with, there are a series of condensing tubes, all passing through one large outer case of zinc, on which cold water streams, so that a whole row of extractions may be done at the same time. When the condensed liquid drops back into the flask perfectly colourless, the extraction is at an end, and the liquid is rinsed from the flask into a measure, and made up to 250 c.c. As a rule, this liquid is not perfectly clear, and seeing that it must be so before applying the powdered hide, we have next to proceed to :—

2. *The Filtration of the Liquid.*—This is done by means of the apparatus shown in figure 2. A is a short wide tube, having another tube (B) fused into its lower end, B being bent in the form of a syphon. To prepare A for use, a piece of wire-gauze covered by flannel is first dropped in, and then that is followed by a pulp made by macerating filter-paper in distilled water for a few minutes. When A is thus filled, the operator's lips are applied to the end of B, so as to suck out the excess of water and cause the pulp to mat together. The mouth of A is then closed by an india-rubber cork, through which passes a bent tube (C), which is in turn attached by means of an india-rubber tube, about 2 ft. long, to the bottom outlet of the bottle D, this bottle being placed on a stand as shown. The liquid to be filtered is poured into

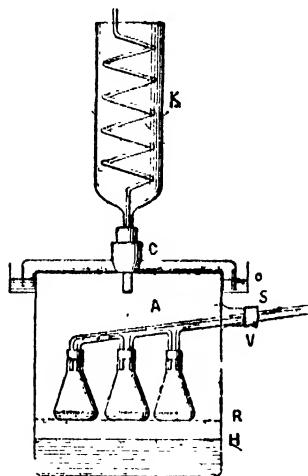
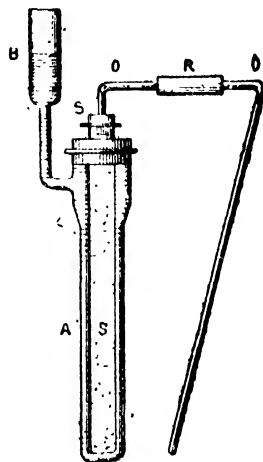


the bottle D, and the tube B is hooked over a receiving jar. The liquid now begins to

filter, and the rapidity of filtration is regulated by altering the height of the bottle. The first 20 c.c. that pass through are rejected, and the remainder is used for the next step of the process.

### 3. *Extraction of the Tannin by the Powdered Hide.*—

This is done in the apparatus shown in figure 3, and known as the "Tannimetre Jean." A is a glass tube, closed at the bottom, and having a cylindrical funnel and bent tube (B) fused into its upper part. Inside A an inner tube (S) is fixed by means of an india-rubber ring. The tube S is in turn closed by an india-rubber stopper, through which passes the bent tube O. This tube is joined to a corresponding portion by means of a long cork (R), so that, when O is turned down, the whole forms a syphon with the inner tube S. By turning O in R we can establish or stop the syphon action at pleasure. To prepare the apparatus for use, we close the end of S with a piece of wire-gauze covered with flannel, and we then pack it with the powdered hide, and place it in position inside A as shown. The liquid to be exhausted is introduced into the funnel B *very slowly*, so that it is gradually sucked up into S by capillary action, the tube O being at the same time kept turned up to prevent any action of the syphon. When the liquid in the two tubes A and S have both reached the level of the point where the funnel tube is fused into A, some more of the liquid is poured into the funnel B, so as to raise the level of liquid just short of the bend in O, and the whole allowed to stand for one hour. At the expiration of this time, the funnel is nearly filled with the liquid, and the syphon having been turned down, filtration is established and continued until 40 c.c. have dropped from the longer limb of O. If the apparatus has worked properly, the filtrate should be limpid, almost colourless, and should not



give a precipitate with gelatine. The powder used is the article produced at the Imperial Tannery in Vienna, and can be purchased with the apparatus from Demichel at Paris. When a new lot of powder is purchased, it is necessary to make a blank experiment by charging the "tannimetre" therewith, and using distilled water instead of a tannin solution, so as to obtain an extract. By now evaporating 25 c.c. of this liquid and weighing the residue, we obtain the check for the particular lot of hide powder. Such check is, however, very constant, and is .016 grams. for the ordinary powder containing 15.15 per cent. of moisture.

4. *Obtaining and Weighing the Residue.*—25 c.c. of the solution that has not passed through the tannimetre, and another 25 c.c. of that which has so passed, are each evaporated in a weighed flat-bottomed glass capsule at

212° F., and the dry residues are weighed. The difference between the two weights, less the check, gives the amount of "assimilable tannin," and this result, multiplied by 10, gives the quantity in the weight taken for analysis, and, lastly, this is calculated to percentage. The apparatus actually employed for drying the residues is shown in figure 4. It works with great rapidity, and is manifestly adapted to the obtaining of the residue of any fluid of which a number of samples are to be done at the same time. It is a copper bath (A) with amovable top (C), through which passes the end of an upright condenser. A trough containing sand goes all round the top of the bath, so that, when the lid is put on, it fits steam-tight. Water is put in up to the level (H), and immediately above there is a sheet of wire-gauze (R) for the articles to stand on. The liquid, of which the residue is to be obtained, is placed in a tarred, flat-bottomed glass flask, the base of which is about 2.5 in. in diameter. When a series of flasks have been charged they are closed by india-rubber corks, through which pass the arrangement of tubes shown in the drawing, such tubes projecting through a side tubulure (S) specially arranged for the purpose. The water in the bath having been set to boil, one of the glass tubes projecting through S is attached to an empty flask, and this is in turn connected with a water vacuum pump. The whole of the flasks being immersed in vapour at 212°, and all the vapour being drawn off as fast as it forms, the evaporation proceeds with extreme rapidity. When no more liquid condenses at the extremity of the exhausting tube, the inlet tube is attached to an air-drying arrangement, so that a current of perfectly dry air is caused to pass over the residues, and the absolute desiccation is rapidly achieved.

#### ON WAX ANALYSIS.

By M. H. ROTTER.\*

THE method most commonly employed for the analysis of beeswax is based upon Köttstorfer's process for the analysis of fats by two successive saponifications, as follows :— Five grams. of the wax are warmed with 20 c.c. of alcohol (of 95°) until they fuse, and a few drops of alcoholic solution of phenol-phtalein having been added, the whole is shaken and titrated, while still warm, with semi-normal solution of potassium hydrate, delivered from a burette divided into .5 c.c. From the result of this experiment the quantity of potash, in millegrammes, necessary to saturate the cerotic acid contained in one gramme of the wax is calculated and is put down as the first number. Twenty c.c. more of the potash solution are then run in, and, the flask having been connected with an upright condenser, the whole is heated until entire saponification has taken place. When this is attained, the flask is brought under a burette containing semi-normal hydrochloric acid, and titrated until the colour is just discharged. The number of c.c. of hydrochloric acid so used deducted from 20 gives the c.c. of the potash solution used up in the act of saponifying the myricyl palmitate ; from this is calculated the amount of potash in millegrammes necessary for one gramme of the wax, and the figure so obtained is called the second number. Finally, the first and second numbers are added together to obtain the third number.

Numerous researches have shown that in pure yellow beeswax the first number is

\* *Monit. Scient.*

20 millegrammes (or between 19 and 21); that the second number is 75 millegrammes (or from 73 to 76); while the third number is 95 (or from 92 to 97). The relation between the first and second numbers in genuine wax is as 1 to 3·7 on the average, but may vary between 1 to 3·6 and 1 to 3·8, and the third number must not be departed from in any genuine sample.

Recently, G. Buchner has analysed a series of samples, and has given the following results, tending to show that this theory breaks down when we have to deal with wax which has been bleached by chemical means. The following are Buchner's results:—

|                                 | 1st number. | 2nd number. | 3rd number. | Relation. |
|---------------------------------|-------------|-------------|-------------|-----------|
| Yellow wax .. .. .              | 20·2        | 73·8        | 94·8        | 1·3·65    |
| Naturally-bleached wax .. .. .  | { 19·91     | 75·0        | 94·9        | 3·76      |
|                                 | { 19·80     | 74·9        | 94·7        | 3·78      |
| Chemically-bleached wax .. .. . | 21·97       | 76·4        | 98·37       | 3·47      |
|                                 | { 22·00     | 75·9        | 97·9        | 45        |
| Ditto .. .. .                   | { 24·2      | 74·8        | 99·0        | 09        |
|                                 | { 23·8      | 74·5        | 98·3        | 13        |
|                                 | { 23·9      | 71·5        | 98·4        | 3·11      |

From these figures Buchner concludes that the standard relation in chemically-bleached samples must be taken as 1 to 3·2.

To test the accuracy of these results some experiments have been done in the laboratory at Helfenberg. Two varieties of genuine yellow wax were started with, and each having been divided into two parts, the one was bleached by the charcoal process and the other by potassium permanganate. The results obtained from these undoubtedly pure samples contradicted those of Buchner, and fully confirmed the original view. They were as follows:—

|                                    | Density. | 1st number. | 2nd number. | 3rd number. | Relation. |
|------------------------------------|----------|-------------|-------------|-------------|-----------|
| Yellow wax .. .. .                 | 0·966    | 19·6        | 74·0        | 93·6        | 3·77      |
| Wax bleached by charcoal .. .. .   | 0·963    | 20·1        | 71·0        | 94·1        | 3·68      |
| " " " K MnO <sub>4</sub> .. .. .   | 0·963    | 18·1        | 72·8        | 90·9        | 4·00      |
| Yellow wax (second sample) .. .. . | 0·964    | 20·1        | 74·8        | 94·9        | 3·72      |
| Wax bleached by charcoal .. .. .   | 0·963    | 19·6        | 74·0        | 93·6        | 3·77      |
| " " " KMnO <sub>4</sub> .. .. .    | 0·964    | 19·1        | 74·0        | 93·1        | 3·87      |

The figures thus obtained showed that the process of bleaching does not increase the specific gravity of wax, as some observers have pretended, and also that the three characteristic numbers are no larger, and are comprised within the same limits as those of ordinary yellow wax. I have lately also had occasion to analyse white wax chemically-bleached by the acid process, and the following are the results I obtain:—

| Specific gravity. | 1st number. | 2nd number. | 3rd number. | Relation. |
|-------------------|-------------|-------------|-------------|-----------|
| 0·966             | 20·2        | 76·7        | 96·9        | 3·79      |

These numbers also contradict Buchner's hypothesis, and I am afraid that the so-called pure white wax with which he was supplied was scarcely what it should have been. It is necessary to be very cautious in accepting commercial descriptions, as is shown by the following analysis of two samples of white wax, sold as of a superior quality, but which were evidently very far from meriting the epithet:—

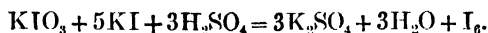
|                    |       |       |
|--------------------|-------|-------|
| 1st number .. .. . | 29·7  | 31·46 |
| 2nd number .. .. . | 87·5  | 76·66 |
| 3rd number .. .. . | 117·2 | 99·1  |
| Relation .. .. .   | 2·9   | 2·14  |

In conclusion, I would urge that there is no reason for adopting any different numbers for judging the purity of white wax to those employed in the examination of yellow.

## ESTIMATION OF ALKALIES AND ACIDS BY MEANS OF IODINE.

BY MAX GRÖGER.\*

THE principle of this process is the action of sulphuric acid on a mixture of potassium iodide and potassium iodate, which is represented by the equation—

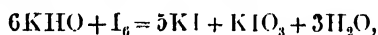


Alkaline solutions are first mixed with excess of sulphuric acid and then with a solution of potassic iodate and iodide (which I will now simply call the iodine solution); acids are at once mixed with the iodine solution, and in both cases the liberated iodine is determined. What we want is a  $\frac{n}{10}$  solution of sodium thiosulphate,  $\frac{n}{10}$  sulphuric acid, and a perfectly neutral solution of the iodine.

The thiosulphate: 25 grammes of the crystallised salt are dissolved in a litre of water. Although the exact strength of the solution can be determined by a known weight of pure iodine, I prefer to operate as follows: About 15 grammes of pure potassium iodate is accurately weighed, dissolved in a little water, mixed with about 1 gramme of pure potassium iodide and acidified with hydrochloric acid. The thiosulphate is then run in until the solution is decolorised, starch solution being finally used as indicator.

The sulphuric acid: 5 grammes of concentrated sulphuric acid are diluted up to a litre. A measured quantity is then mixed with excess of the neutral iodine solution and the liberated iodine determined as usual.

The iodine solution: By dissolving iodine in potash ley a solution is obtained which contains the proper proportion of iodide and iodate—



but one does not succeed in getting a perfectly neutral solution in this manner. If to the warm ley (free from carbonic acid) iodine is added as long as the solution remains colourless, it remains strongly alkaline. If, on the other hand, iodine is added until the fluid is dark brown, and the whole is then thoroughly boiled, the fluid certainly becomes neutral, but always contains some free iodine. It is therefore the best plan to prepare perfectly neutral solutions of potassium iodide, and ditto iodate, and to mix them in the proper proportions. In airtight bottles the mixture may be kept unchanged, but in contact with air the carbonic acid gradually liberates iodine, and the mixture becomes yellowish and also faintly alkaline. It is therefore better to keep both solutions separately, and only to mix just before use. The solutions used in my experiments respectively contained 4 grammes of potassium iodide and 24 grammes of iodate in 100 c.c. When equal volumes were mixed a half normal solution was obtained. It is not necessary to know its exact strength.

*Estimation of Caustic Alkalies.* 50 c.c. of the watery solution (about  $\frac{n}{10}$  strength) were mixed with excess of  $\frac{n}{10}$  sulphuric acid, then with 5 c.c. of the iodine solution, and titrated as usual with thiosulphate. The difference in c.c. of acid and thiosulphate equals the amount of acid required to neutralise the alkali. I also estimated the alkali with acid, using litmus or phenol-phthalein as indicator.

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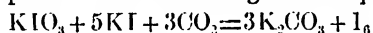
\* *Zeitschr. f. Angew. Chemie*, No. 12, 1890.

| Solution of.    | C.C.s OF ACID REQUIRED. |         |                   |
|-----------------|-------------------------|---------|-------------------|
|                 | Iodine process.         | Litmus. | Phenol-phthalein. |
| KHO             | 39·85                   | 39·80   | 39·85             |
| "               | 27·05                   | 27·03   | 27·05             |
| NaHO            | 42·40                   | 42·42   | 42·40             |
| "               | 35·35                   | 35·30   | 35·30             |
| NH <sub>3</sub> | 31·55                   | 31·50   |                   |
| "               | 48·20                   | 48·25   |                   |

*Estimation of Alkaline Carbonates.*—First of all I investigated the action of free carbonic acid on the iodine solution. A litre of distilled water, saturated with carbonic acid, evolved by ignition of sodium bicarbonate, showed on titrating with baryta water, 1·389 gramme of carbonic anhydride. This carbonic acid solution was now mixed with 20 c.c. of the iodine solution, and from time to time 50 c.c. were titrated with the thiosulphate, with the following results:—

| Directly after mixing | ·18 c.c. <sup>n</sup> / <sub>10</sub> thiosulphate. |
|-----------------------|---|
| " 5 minutes           | ·24 "   |
| " 10 "                | ·27 "   |
| " 15 "                | ·30 "   |
| " 30 "                | ·54 "   |
| " 60 "                | ·72 "   |
| " 2 hours             | ·90 "   |
| " 3 "                 | ·96 "   |
| " 24 "                | 1·68 "  |
| " 48 "                | 1·86 "  |
| " 72 "                | 1·92 "  |
| " 120 "               | 1·92 "  |

The carbonic acid therefore decomposes the iodine solution quickly at first, and gradually slower and slower, until after three days the action completely ceases. The decomposition is very incomplete. Then according to the equation



50 c.c. of this carbonic acid solution ought to have used 31·58 c.c. thiosulphate.

If the solution of an alkaline carbonate is mixed in the cold with an excess of <sup>n</sup>/<sub>10</sub> acid, mixed with iodine solution and titrated with thiosulphate, the liquid after remaining colourless for a moment, rapidly gets blue again. If the thiosulphate is again added a drop at a time, the fluid will get each time blue again, and this keeps on for about an hour. If, however, so much thiosulphate is added that the fluid remains colourless for a few seconds, the results do not materially differ from those obtained by the usual processes.

50 c.c. of solution of alkaline carbonate were mixed in the cold with 50 c.c. of <sup>n</sup>/<sub>10</sub> sulphuric acid, then after addition of 5 c.c. iodine solution, titrated with thiosulphate until the liquid was colourless. After standing for thirty minutes the blue colour was once more destroyed by more of the reagent. Another 50 c.c. were mixed with 50 c.c. of acid, boiled to expel carbonic acid, and titrated back with <sup>n</sup>/<sub>10</sub> potash.

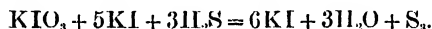
| Solution of                     | C.C.s OF ACID CONSUMED. |                                      | Phenol-phthalein. | Litmus. |
|---------------------------------|-------------------------|--------------------------------------|-------------------|---------|
|                                 | Direct.                 | Iodine process.<br>After 30 minutes. |                   |         |
| K <sub>2</sub> CO <sub>3</sub>  | 43·82 ..                | .. 43·65                             | 43·91             | 43·90   |
| Na <sub>2</sub> CO <sub>3</sub> | 28·06 ..                | .. 27·80                             | 28·15             | 28·15   |
| Am <sub>2</sub> CO <sub>3</sub> | 29·54 ..                | .. 29·49                             | —                 | 29·56   |
| KHCO <sub>3</sub>               | 48·08 ..                | .. 47·58                             | 48·15             | 48·17   |
| NaHCO <sub>3</sub>              | 46·87 ..                | .. 46·35                             | 46·96             | 46·99   |
| AmHCO <sub>3</sub>              | 32·90 ..                | .. 32·46                             | —                 | 33·00   |



The influence of the carbonic acid is plainly visible from this table. The results obtained on titrating immediately after mixing are practically the same as those obtained by the litmus process, but those obtained after allowing the mixture to stand for thirty minutes are too low, more particularly in the case of the bicarbonates.

If, however, the iodide solution is added after all carbonic acid has been expelled by boiling and the fluid got cold again, perfectly concordant results may be obtained. For delicate analyses this course is therefore to be recommended.

*Estimation of Alkaline Sulphides.*—Hydrogen sulphide is completely decomposed by iodine solution :



If, therefore, solutions of the alkaline sulphides or hydrogen sulphides are mixed with a known excess of  $\frac{n}{10}$  acid, and then with a sufficiency of iodine solution, the liberated iodine may be determined by means of thiosulphate, but even when a slight excess of the latter has been added the liquid still has a dirty blueish colour, because the separated sulphur encloses some of the iodide of starch. I made experiments with solutions of caustic alkalies before and after saturation with hydrogen sulphide, with the following results :—

| 50 c.c. solution of | C.C.S OF ACID USED. |    |  |       |
|---------------------|---------------------|----|--|-------|
|                     | Direct.             |    | After saturating with $\text{H}_2\text{S}$ . |       |
| KHO                 | 30.04               | .. | ..   | 29.36 |
| "                   | 42.30               | .. | ..   | 41.90 |
| NaHO                | 27.59               | .. | ..   | 27.03 |
| "                   | 44.25               | .. | ..   | 43.85 |

If, however, the hydrogen sulphide is first expelled by boiling, the results are satisfactory, as will be seen from the following series of experiments. The results were checked in the usual way.

| Solution of             | C.C.S OF ACID CONSUMED. |         |                   |
|-------------------------|-------------------------|---------|-------------------|
|                         | Iodine process.         | Litmus. | Phenol-phthalein. |
| $\text{K}_2\text{S}$    | 25.75                   | 25.70   | —                 |
| $\text{Na}_2\text{S}$   | 32.04                   | 32.06   | 32.04             |
| $\text{Am}_2\text{S}$   | 39.82                   | 39.79   | —                 |
| KHS                     | 48.31                   | —       | 48.25             |
| NaHS                    | 19.57                   | —       | 19.60             |
| AmHS                    | 45.55                   | 45.55   | —                 |
| $\text{K}_2\text{S}_3$  | 28.20                   | 28.06   | —                 |
| $\text{Na}_2\text{S}_3$ | 32.18                   | 32.15   | 32.18             |
| $\text{Am}_2\text{S}_3$ | 17.05                   | 17.00   | —                 |

The sulphur, which separates on the addition of acids to polysulphides, does not interfere with the titration.

If, therefore, a very accurate analysis is wanted, it is best to expel the hydrogen sulphide by boiling, but if its amount is but very small this is not necessary. The fading of the blue colour is, as a rule, easily to observe, even in somewhat dark-coloured liquids, such as wood ash lye, soap lyes, ammoniacal liquid from gasworks, etc., which makes the iodine process preferable to the titrating with litmus or methylorange. Although this last indicator has got much in favour lately, I must confess I have some difficulty in noticing the end reaction, if the fluid under examination is somewhat yellowish or brownish.

*Estimation of Acids.*—50 c.c. of acid solution were added to 10 c.c. of iodine solution, and the liquid at once titrated with thiosulphate. A check was made by  $\frac{n}{10}$  potash :

| Solution of                    | USED.                 |                 |
|--------------------------------|-----------------------|-----------------|
|                                | C.C. of thiosulphate. | C.C. of potash. |
| H <sub>2</sub> SO <sub>4</sub> | 41.90                 | 11.80           |
| "                              | 17.55                 | 17.55           |
| HCl                            | 28.14                 | 28.20           |
| "                              | 35.70                 | 35.70           |
| HNO <sub>3</sub>               | 42.87                 | 42.92           |
| "                              | 15.05                 | 15.10           |

Organic acids act but very slowly in the cold, requiring some 24 hours. With acetic acid the action was not even then complete, 50 c.c. of a weak solution requiring 38.55 c.c. instead of 40.3 c.c. thiosulphate. As, however, heating very much promotes the action, I fancy good results may be obtained by first distilling off the liberated iodine. If successful it will be an excellent process for determining the acidity of wines, beers, and other dark-coloured liquids.

#### REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

ASSAY OF GUM ARABIC AND GUM SENEGAL. BY LIEBERMANN. (*Chem. Zeit.*, No. 41, 1890). 1. Gum arabic forms round or angular, colourless, yellowish or brownish lumps, which strongly refract the light, and look as if they possessed a crystalline structure. Owing to the disturbed state of trade in the Soudan, much of the gum arabic nowadays imported is partly, or even totally, composed of gum senegal.

2. Gum senegal forms either colourless or yellowish lumps, somewhat whitish on the surface (resembling corroded glass), the interior of which is, however, clear and lustrous. The lumps are generally longish, straight or bent, vermicular or cylindric. Sometimes they look as if small lumps have deposited round a larger one. They have to a certain extent the shape of mulberries. If, therefore, the sample is not in powder or too small lumps the very appearance will tell the fraud.

3. Both varieties are completely soluble in water; there only remains small particles of wood, which, in samples of gum arabic, are generally reddish, but blackish in the gum senegal. These woody particles are found even in the superior kinds of the gum. Other gums, like cherry gum, are only partly soluble in water. There remains a jelly which only dissolves on prolonged boiling.

4. The watery solution of both gums gives with potash-ley and a few drops of solution of copper sulphate blueish precipitates; but with gum arabic the precipitate is more abundant, sticks together, and rises to the surface of the fluid. The precipitates are not dissolved on heating and do not reduce the copper.

5. Dextrine solution also gives a blue precipitate, but this dissolves completely on warming to a clear dark-blue fluid. On prolonged boiling the copper gets completely reduced.

6. Heated for a long time with dilute potash, gum arabic or dextrine turn amber-yellow, whilst gum senegal scarcely colours at all.

7. Mixtures of the two gums behave towards potash and copper sulphate like pure gum senegal, but on boiling with potash alone the mixture turns amber-yellow.

8. Mixtures of gum arabic and dextrine behave towards potash and copper sulphate like pure gum, but on long boiling reduction takes place if at least the amount of dextrine is not too small.

9. To detect *small* quantities of dextrine the liquid must, after a slight warming, be filtered before boiling.

10. In similar manner the separation must be performed when both kinds of gum are present, as well as dextrine. The cupric precipitate containing both gums is washed with distilled water, dissolved in a little dilute hydrochloric acid, and mixed with a large excess of spirit. After standing for a day, the transparent deposit is dried, then dissolved in hot water, and tested according to 4 and 6.

The assay of gum arabic may also be prepared according to the following scheme:—

(A). The appearance of the sample when not in powder. (See 1 and 2.)

(B). Try the solubility of the powdered sample in warm water. (See 3.) If the sample is but partially soluble, and leaves a jelly-like mass, there is no doubt cherry gum. If practically soluble, the solution is mixed with excess of potash and a little copper sulphate, gently heated and filtered:

(a). The filtrate is treated for dextrine according to 9.

(b). Precipitate is treated as described in 10. The deposit will either agglomerate and float, or remain suspended in the fluid. In the first case there is gum arabic, and the original fluid will turn amber-yellow with potash. In the second case if there is no colour got with potash, there is only gum senegal.

It has been said gum senegal is more hygroscopic than gum arabic. To make sure the author dried both specimens at 105° C., and then exposed them for twenty-four hours to moist air, when gum arabic was found to be even a trifle more hygroscopical than the gum senegal.

L. DE K.

A NEW INDICATOR: (A) NAPHTOL-BENZEIN. R. LALOZIECKI. (*Chem. Zeit.*, No. 37, 1890).—The author prepares this substance by mixing two molecular quantities of (a) naphtol with one benzol trichloride, after adding some benzol to mitigate the action. After standing for twenty-four hours the whole is heated up to 40° C., and the benzol, with the excess of the trichloride, driven off in a current of steam. The product is then purified by repeated solution in soda lye, and precipitation with hydrochloric acid. In volumetric analyses ten or twenty drops of its 1 per cent. spirituous solution is added to the fluid until the acid changes the liquid from green to orange, or the alkali from orange to green. In the latter case it is, however, preferable to add a slight excess of alkali, and titrating back with acid.

The change is plainly visible, even with artificial light.

L. DE K.

A DELICATE REAGENT FOR SOME ESSENTIAL OILS. A. IHL. (*Chem. Zeit.*, No. 27, 1890).—Pyrol acts very characteristically on the incrustating material of wood. The author thought of trying its action on ethereal oils, and obtained the following results:—

Cinnamon oil: A very weak alcoholic solution of this oil gives with dilute alcoholic solution of pyrol, mixed with hydrochloric acid, first a yellowish-red colour, which soon turns dark red, and finally deposits a dark coloured substance. This test is a delicate one for both pyrol and the oil. Oil of cloves: This, when mixed with a dilute alcoholic solution of pyrol and some hydrochloric acid, gives a splendid carmine colour. The same occurs with pimento oil. Oil of sassafras gives a splendid rose-red colour. Spearmint oil gives but a faint reddish colouration, and aniseed oil only a yellowish colour. The author thinks these oils are closely related to the woody substance. L. DE K.

SIMPLE METHOD FOR THE ESTIMATION OF EXTRACTS IN WINES. ED. LASZLO. (*Chem. Zeit.*, No. 27, 1890).—It has several times been remarked how important it would be to everywhere determine the extract of wine by the same process. Now, this is done in nearly every country by a different method, causing different results, and consequently great dissatisfaction. In Austria, and also in Germany, the direct process is in vogue, although, as has often been remarked, the results do not really represent the true amount of extract, but simply the percentage happening to be left after drying for two hours and a half. The author gives a few instances of the unreliability of this method. Just to mention one: Two wines, having exactly the same specific gravity and the same percentage of alcohol, still showed a difference of .24 per cent. in extract. These wines were analysed by the same chemist. Even the lowest result was still .21 per cent. in excess of the calculated quantity. A process which gives such contradicting results cannot really be tolerated.

As regards the indirect process, the author refers to the pamphlet of B. Haes, but also calls attention to Pohl's thermo-areometric test. The extract gravity is calculated from the percentage of alcohol, and the present gravity of the sample (extract gravity = present gravity + [1 - alcoholic gravity]). Pohl used for his alcohol estimations his vaporimeter, which gave varying results, so his extracts were therefore faulty; and, although we now possess Malligand's vaporimeter, the process seems to have got quite out of use. The author now uses a very accurate hydrometer, which enables him to read off .1 per cent. of alcohol. It shows percentage of alcohol by volume, and must be used at 15° C. If used for wine it will, of course, show the less alcohol, as there is more extract. The difference between real and apparent alcohol may serve, of course, as a basis of calculation of the extract.  $E = f(a - s)$ , in which equation  $E$  represents the amount of extract in 100  $A$ ;  $A$  the actual amount of alcohol by volume, determined, say, by distillation;  $S$  the apparent amount of alcohol found by the hydrometer; and  $F$ , a correction which the author proposes to fix as .32.

If the sample should be heavier than water, the author uses a Billings' saccharometer (hydrometer), but calculates its percentages by weight to ditto by volume. In analysing sweet wines, he therefore multiplies the alcohol by volume with .32, and adds the saccharometer degrees, calculated to volume. The test analyses are very satisfactory. Of a sample containing 12.0 per cent. of alcohol and 2.5 per cent. of extract, the latter was found to be 2.52 by the author's process. The apparent percentage of alcohol was 4.1. L. DE K.

DETECTION OF STEARIC ACID AND PARAFFIN IN WAX. H. RÜTTGER. (*Chem. Zeit.* No. 37, 1890).—The author criticises the various methods from time to time proposed. Regnard's process: The sample is boiled with water and then allowed to cool. If stearic acid is present, the watery fluid will slightly redden blue litmus paper. This chemist, however, confesses that the acidity may, in reality, be caused by traces of sulphuric acid

used in bleaching the wax. He also proposes to boil the sample with lime-water in a flask attached to a reflux condenser, when, if stearic acid is present, a flocculent deposit of calcium stearate forms. Geith also uses the lime-water test, but does not mention anything about the precipitate; only says the lime-water loses its alkalinity. The author's experience of this process is that a precipitate forms at first, but disappears on boiling. It depends on the strength of the lime-water or on the amount of stearic acid whether the watery fluid will present an alkaline, or even an acid, reaction. Hayer shakes a chloroform solution of the sample with twelve volumes of lime-water very suddenly. If stearic acid is present, there forms a lime soap in dendritic and granular ramifications, whilst the chloroformic fluid neatly separates as a white emulsion. The author cannot recommend this modified process. Fehling says: As pure wax contains cerotic acid, which, in its behaviour to caustic and carbonated alkalies, resembles stearic acid, the test with lime-water cannot succeed if the adulteration is below 10 per cent. He recommends the following plan:—The sample is boiled for five minutes with twenty times its weight of alcohol, and then allowed to cool. After standing for a few hours, the liquid is filtered off and mixed with water. If the sample was pure there will be but a faint opalescence, as cerotic acid, although soluble in boiling alcohol, almost completely separates out on cooling; but if as little as 1 per cent. of stearic acid is present it will cause a decided flocculent precipitate. The author finds this a most elegant and reliable process. Benedict boils the sample with solution of sodium carbonate, when, if stearic acid is present, the alkaline fluid will, on cooling, gelatinise. The author finds this process to be less safe than the previous one, especially if the adulteration is rather small.

*Detection of Paraffin and Ceresin.* Landolt's Process:—Fuming sulphuric acid completely destroys wax; paraffin is not attacked. The sample is heated in a porcelain dish with this acid in excess, when, after some time, the paraffin will float on the top of the fluid. This not very elegant and very uncertain process is not of much use nowadays, as the kind of paraffin now employed for wax adulteration is also destroyed by the acid. Wagner calculates the amount of paraffin from the specific gravity. He argues: Genuine wax has a constant specific gravity, whilst the various kinds of paraffin do also not greatly differ in gravity from each other. He gives the following table:—

| Wax. | Paraffin. | Specific gravity. |
|------|-----------|-------------------|
| 0    | 100       | 871               |
| 25   | 75        | 893               |
| 50   | 50        | 920               |
| 75   | 25        | 942               |
| 80   | 20        | 948               |
| 100  | 0         | 969               |

Pure wax (free from paraffin) ought to sink in spirits of wine of 961 specific gravity. Donath, after making sure that no other adulterations are present, also calculates the amount of paraffin from the specific gravity. If the gravity of the sample should fall below 960, he takes the presence of paraffin for granted. Buchner made several determinations of the specific gravity of various kinds of ceresin, and found it to vary from 858 to 901. Wax containing ceresin still floats on spirits of wine of 950 specific gravity. For the chemical detection, he boils the wax with alcoholic potash (1-3), when paraffin and ceresin, not being saponifiable, will float on the surface. Hager heats 2 grams. of the wax with 5 c.c. solution of common soda, shakes well, and adds 6 c.c. of benzol, when an emulsion forms. After standing for an hour in water of 50° C., two layers form. If the wax is pure, the benzol will, after cooling, be almost clear; but in the presence of paraffin it will be thickish and turbid. Sedna puts the wax shavings with twenty times their amount of ether for half a day. Wax scarcely dissolves, but the paraffin does. Of the ethereal residue five-sixths is called paraffin.

L. DE K.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

### ON SOME RECENT ADVANCES IN OUR KNOWLEDGE OF THE SUGAR GROUP.

By WALTER J. SYKES, M.D., D.P.H., F.C.S., ETC.

(Read at Meeting, June, 1890.)

THE synthesis of the sugar group, a process so intimately connected as it is with the physiology of plant life, has naturally formed an attractive subject of investigation amongst chemists. Numerous attempts have been made from time to time to form these bodies synthetically, but hitherto only a small measure of success has attended the efforts made in this direction. Quite recently, Dr. Emil Fischer has solved this problem in a most brilliant and satisfactory manner, since he has not only synthesised from the elements glucose and the whole mannitol group of sugars, but has also discovered new members of this group, of the existence of which we previously knew nothing. His labours throw considerable light on the molecular constitution of the individual members of the group as well. My paper of this evening is a brief *resume* of his important work in this direction.

The ordinary hexa-hydric alcohol mannitol  $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot \text{CH}_2\text{OH}$ , obtained by extraction with alcohol from ordinary manna, yields upon limited oxidation with  $\text{HNO}_3$  a body very similar in its properties to glucose. It reduces Fehling, ferments in contact with beer yeast, and rotates the polarised ray to the right, though not to such a wide angle as glucose. This body mannose is the aldehyde of mannitol, and has the following constitution:— $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot \text{COH}$ . Upon further oxidation with Br it yields the corresponding mannonic acid  $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot \text{COOH}$ . If a solution of this

acid be evaporated to a syrupy consistence, a molecule of water is disengaged, and the lactone or anhydride of the acid produced  $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CH}\cdot\overset{\text{O}}{\text{C}}(\text{CHOH})\cdot\text{CO}$ .

This body crystallises in stellate groups of colourless needles, melts at  $149$  to  $153^\circ \text{C}$ ., and has a specific rotary power of  $[\alpha]_D + 53.81$ . Its solution has a neutral reaction; it, however, readily decomposes carbonates, and forms the corresponding mannonates.

Killiani some years since obtained by boiling certain gums with dilute  $\text{H}_2\text{SO}_4$  a penta-hydric aldehyde (sugar) to which he gave the name arabinose. This sugar upon treatment with  $\text{HCN}$  yields the cyan-hydrin, and this in its turn upon treatment with  $\text{Ba}(\text{HO})_2$  yields the acid of the alcohol of the next degree higher in the series. This he called arabinose-carboxylic acid; it has the same composition as the mannonic acid mentioned above. On evaporation the arabinose-carboxylic acid yields its lactone.

In this method of Killiani's we have obviously a method of passing up the alcohol series, from lower to higher, and to which I shall have to revert further on.

The lactones of the mannonic and arabinose-carboxylic acids have obviously the same structural formulæ, and are so similar in other respects that they must have been considered identical, had not their optical properties differed. Mannonic acid lactone polarises  $[\alpha]_D + 53.81$ , the other lactone  $-54.8$ ; in other words, making allowance for experimental error, these two bodies possess equal and opposite optical activities, and may, therefore, be looked upon as two optically opposed isomerides like the dextro and laevo-tartaric acids. This is the first instance observed of the occurrence of such a relation in the sugar group. If such be the case, it is obvious that in a solution of equal quantities of the optically opposed lactones, combination ought to take place, and an inactive lactone be produced, as in the parallel case of the two tartaric acids, which under similar conditions unite and form racemic acid. The experiment was tried, and found perfectly successful; an inactive lactone was produced which could only be split up again into its optically opposed components under special conditions.

All these lactones by reduction with sodium amalgam can be converted first into their aldehydes (sugars), and by further reduction into the corresponding alcohols. Upon dissolving  $\text{BaCO}_3$  in a solution of the lactones, the  $\text{Ba}$  salt of the corresponding acid is produced, and from this salt the acid can be liberated. In this manner we obtain by reduction from mannonic acid lactone, the corresponding aldehyde (mannose), and the alcohol. These and the acid all polarise to the right. From arabinose-carboxylic acid lactone we obtain a similar series, all polarising to the left, from a mixture of the two lactones a series optically inactive. Hence there can be no doubt that arabinose-carboxylic acid lactone is left mannonic acid lactone, and for the remainder of the paper I shall designate it as such, and also the mixed lactone as inactive mannonic acid lactone.

It has been found that phenyl-hydrazine forms an important series of compounds with several members of the sugar group, and as one of these combinations has proved the key to the solution of the problem of the synthetical formation of the sugar group, it will be advisable to devote a few minutes to a description of these compounds.

Phenyl-hydrazine is a body having the composition  $\text{Ph}^* - \text{NH} - \text{NH}_2$ ; it possesses

---

\*  $\text{Ph} = \text{C}_6\text{H}_5$ , the symbol for the radical of benzene.

basic properties, and readily unites with HCl and acetic acids. It forms with aldehydes and ketones a class of stable bodies [thus with aldehyde the following reaction takes place:— $\text{CH}_3\text{COH} + \text{Ph} - \text{NH} - \text{NH}_2 = \text{Ph} - \text{NH} - \text{NCH}(\text{CH}_3) + \text{H}_2\text{O}$ .] When added to an aldehyde member of the sugar group in the proportion of one molecule to one molecule, an exactly similar reaction takes place. Thus, if one molecule of the aldehyde mannose be added to one of phenyl-hydrazine, the compound  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_5$  is formed. To this series of bodies Fischer gives the name phenyl-hydrazones or more shortly hydrazones. They are for the most part colourless bodies, mostly soluble in water, and are occasionally of diagnostic value. Under the influence of strong HCl they split up into phenyl-hydrazine and the original aldehyde (sugar).

When, however, three molecules of phenyl-hydrazine are added to one molecule of an aldehyde or ketone sugar, the following reaction takes place:— $3\text{C}_6\text{H}_5\text{N}_2\text{H} + \text{C}_6\text{H}_{10}\text{O}_6 = \text{C}_1\text{H}_{22}\text{N}_4\text{O}_4 + \text{C}_6\text{H}_5\text{NH}_2 + \text{NH}_3 + 2(\text{H}_2\text{O})$ . In this reaction phenyl-hydrazine plays the part of an oxidiser, two atoms of H being removed; these are not evolved as gas, but react upon the third phenyl-hydrazine molecule, forming aniline and  $\text{NH}_3$ . To this series the name phenyl-glucosazone or shortly glucosazone has been given. They are difficultly soluble bodies, and are extremely useful in the isolation and recognition of the various members of the sugar group, their melting points, solubility, and crystalline forms, differing. They rotate the polarised ray in the reverse direction to that which the aldehyde of the same series does, and may in this way be used for the purposes of discrimination.

Thus if 0.1 gram. of R. mannose-glucosazone be dissolved in 1 c.c. of strong HCl, immediately added to 5 c.c. water and tested in a 10 decimetre tube, it will turn the ray 1.20 to the left.\*

A phenyl-glucosazone treated with strong HCl is resolved into phenyl-hydrazine and a body having the composition  $\text{C}_6\text{H}_{10}\text{O}_6$ , that is, containing two atoms less H than the original sugar. For this class the name glucosone, or, more shortly, osone, has been proposed. They polarise weakly in an opposite direction to the aldehyde sugar of the series to which they belong.

Upon acting on an osone with Zn dust and acetic acid, two atoms of H are attached, and the levulose belonging to the series is formed. The levuloses have the formula  $\text{CH}_2\text{OH} \cdot 3(\text{CHOH}) \cdot \text{CO} \cdot \text{CH}_2\text{OH}$ , and are therefore ketonic bodies. They polarise strongly in the opposite direction to the aldehyde of the same series.

Phenyl-hydrazine also gives a series of very insoluble compounds with the acids of the group; these are distinguished as hydrazides.

Seeing that in one series we have members some of which polarise to the right, some to the left, it is obviously impossible to use the old terms dextro and levo any longer, as confusion must unavoidably arise. To obviate this, Fischer proposes to name all the series according to the rotation of the aldehyde (sugar) member of the series, and for this purpose use the letters R. L. I. to the compounds in it, just in the same manner as we use O. M. P. in the benzene ring compounds. It is extremely awkward to speak of R. levulose, and the name "fructose" is proposed instead, which is simply fruit sugar latinised.

\* The observation must be taken quickly, as HCl, even in the cold, decomposes the compound in three or four hours completely.



The accompanying table gives a summary of the group and its various compounds and derivatives :—

|                                   |             |                                |                                |                    |
|-----------------------------------|-------------|--------------------------------|--------------------------------|--------------------|
| CH <sub>2</sub> OH — Evaporation. |             | CH <sub>2</sub> OH — Oxidation | CH <sub>2</sub> OH — Oxidation | CH <sub>2</sub> OH |
| CHOH                              |             | CHOH — with Br.                | CHOH — with HNO <sub>3</sub>   | CHOH               |
| CHOH —                            | Conversion  | CHOH — Reduction               | CHOH —                         | CHOH               |
| CHOH — O                          | into a salt | CHOH — with Na                 | CHOH — Further                 | CHOH               |
| CO —                              | with a      | CHOH — Amalgam                 | CHOH — reduction               | CHOH               |
|                                   | carbonate   | COOH                           |                                | CH <sub>2</sub> OH |
| R. Lactose.                       |             | Mannonic acid.                 | Mannose.                       | Mannitol           |
|                                   |             |                                |                                | (with borax.)      |

|                 |     |     |     |     |
|-----------------|-----|-----|-----|-----|
| Polarise right. |     |     |     |     |
| I.              | Do. | Do. | Do. | Do. |

|           |     |                            |     |     |
|-----------|-----|----------------------------|-----|-----|
| Inactive. |     |                            |     |     |
| L.        | Do. | Arabinose-carboxylic acid. | Do. | Do. |

|                               |                                       |                             |  |   |
|-------------------------------|---------------------------------------|-----------------------------|--|---|
| Polarise left.                |                                       |                             |  |   |
| With one molecule of Ph-hzin. | CH <sub>2</sub> OH<br>3(CHOH)<br>CHOH | Two molecules Ph-hydrazine. | CH <sub>2</sub> OH Strong HCl<br>3(CHOH)<br>C-N-HN-Ph. | CH <sub>2</sub> OH Reduction<br>3(CHOH) Zn. and A.<br>CO<br>CHO |
| R. Mannose.                   | Ph-hydrazone.                         | CH-N-HN-Ph.                 | Ph-glucosazone.  | Glucosone.  |
|                               |                                       |                             |  | Lævulose.   |

|                |     |     |     |     |
|----------------|-----|-----|-----|-----|
| Polarise left. |     |     |     |     |
| I.             | Do. | Do. | Do. | Do. |

|           |     |     |     |     |
|-----------|-----|-----|-----|-----|
| Inactive. |     |     |     |     |
| L.        | Do. | Do. | Do. | Do. |

Polarise right.

It is evident that if we could form any one of the bodies of the inactive series synthetically from the elements, we could transform it into all the members of that series; and if it were possible to split up any one of these inactive bodies so formed into its optically opposed components, the synthesis of the whole of the members of the group could be accomplished. This has been found possible.

So long since as 1861, Butlerow had observed that formaldehyde in aqueous solution by contact with various bases yielded, by condensation, a sugar-like body, to which he gave the name methylenitan. Loew pursued this investigation further, and found that the various bases differed very much in their power of causing the condensation of formaldehyde. Lead oxide was found to have a remarkably powerful action at a moderately high temperature, even when present in very small quantity. The method which he found to give the best results is as follows :—To four litres of water, containing in solution 40 grams. of formaldehyde, are added half a gram. of magnesium oxide, two or three grams. of magnesium sulphate, and 350 to 360 grams. of granulated lead. The whole is to be kept at a temperature of 60° C. for twelve hours. On evaporation of the fluid, a sweet neutral syrup is left behind, which reduces Fehling, and is capable of undergoing alcoholic fermentation. To this substance Loew gave the name formose.

Fischer obtained, by acting upon acrolein bromide with barium hydrate,\* a sugar-

\*  $2C_3H_4Br_2O + 2Ba(OH)_2 = C_6H_{12}O_6 + 2BaBr_2$ .

like body, which he named *a. acrose*. More recently he was able to form the same body from glycerose obtained in the following manner:—500 grams. of plumbic hydroxide are stirred intimately into 1,000 grams. of 85 per cent. glycerol; to this is added, with constant stirring, two and a half litres of ice-cold alcohol. The lead glyceroxide thus formed is spread in thin layers, placed under a bell glass in proximity with a shallow vessel containing a quantity of Br equal to half the weight of the lead salt. After the Br is absorbed, the product is extracted with alcohol and concentrated in a partial vacuum, when the glycerose remains as a syrup. The syrup is diluted with water and KHO added until the solution contains about one per cent. of the base, on standing for some days, polymerisation takes place, and amongst other compounds *a. acrose* is formed.

He also repeated the above-mentioned Loew's process, and found that Loew's formose was a mixture of various aldehyde and ketone sugars. Upon treating formose with excess of Ph-hydrazine, a mixture of Ph-glucosazones were formed, all of which were, *with one exception, soluble in alcohol or ether*. The insoluble one, on being treated with strong HCl, yielded the osone, which with Zn and A gave *a. acrose*. This body, formed by either of the three processes, afforded, upon reduction with Na amalgam, a body to which he gave the name *a. acritol*, and which only differed from mannitol\* in its optical inactivity. It struck him that this might be inactive mannitol and *a. acrose* inactive mannose. The first conjecture was undoubtedly true, but the second a little removed from the truth, since *a. acrose* turned out to be a levulose. The purified *a. acrose* must naturally, from the mode of its formation, viz., the reduction of the osone, be a levulose; but the original sugar might be either an aldehyde or a ketone. Its formation from glycerose led to the view being entertained that it was an aldehyde. Placing two molecules of glycerose together,  $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{COH} + \text{CH}\text{OH}\cdot\text{CHOH}\cdot\text{COH}$ , it would seem most probable that one of the II atoms in the second  $\text{CH}_2\text{OH}$  would simply step back and unite with the COII group of the first molecule, yielding the aldehyde sugar,  $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot\text{COH}$ . It was found that on treating the original solution in which the sugar had been synthesised with Ph-hydrazine in the cold, no crystalline hydrazone was formed, as is the case with mannose, and that only on heating is a glucosazone yielded. This reaction is characteristic for levulose.

The formation of a sugar allied to grape sugar, by the condensation of formaldehyde, is of great interest, since it has been assumed by several botanico-physiologists that this is the first step in the process of assimilation. By the agency of the chlorophyll cells, the  $\text{H}_2\text{CO}_3$  lost two atoms of O, forming formaldehyde HCOH; three molecules of this polymerise to form a molecule of grape sugar  $\text{C}_6\text{H}_{12}\text{O}_6$ , which by some occult process loses another molecule of  $\text{H}_2\text{O}$  and becomes starch. The synthesis recently described gives considerable confirmation to this view.

If then *a. acrose* be identical with I. levulose, either it or one of its derivatives ought to be able to be split up into their optically active components.† Fermentation with beer yeast was found to ferment away the R. portion and leave the L., but here,

\* In polarising mannitol and its isomerides, borax was invariably added, which considerably heightens their optical activity.

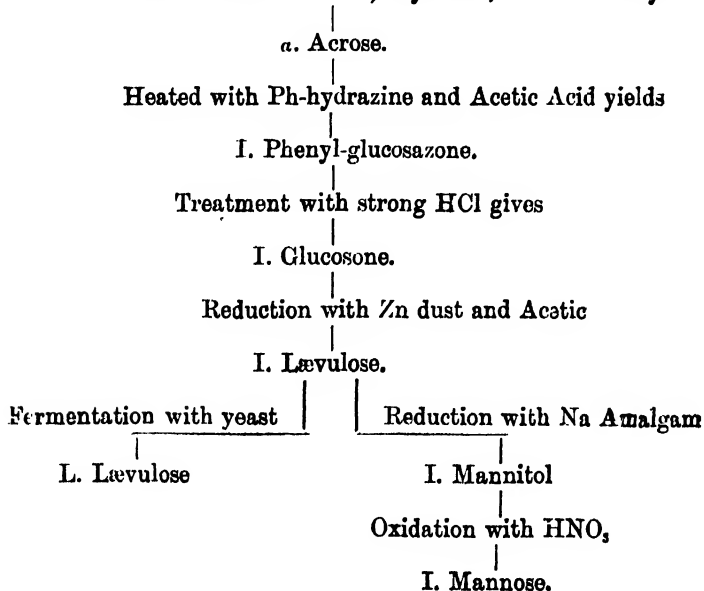
† Levulose, on reduction with Na amalgam, yields the alcohol of the series, mannitol. From this the other members of the series can be obtained in the manner before described.

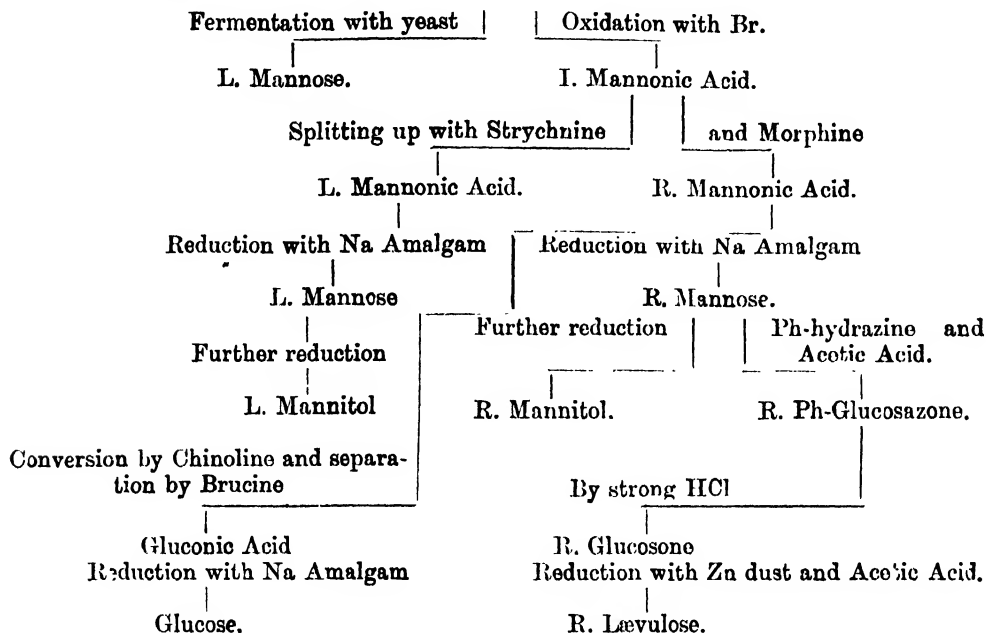
obviously, the R. mannose is lost, so far as further experimentation with it is concerned. In order to effect the splitting up, the acid was subjected to investigation. The mannonic acid salts of various organic bases were tried, such as cinchonine and cinchonidine, etc., but all these were found to be too soluble. Strychnine was found to form a mannonate which, upon evaporation of its aqueous solution, deposited itself as a mass of fine crystalline needles. If these be dissolved in absolute alcohol, a clear solution forms for a moment, but almost immediately, at a boiling heat, the difficultly soluble L. mannonate of strychnine falls. This precipitate, upon purification and removal of the strychnine, yields pure L. mannonic acid, and from this all the L. members of the series can be formed.

The separation is, however, by no means complete, the alcoholic mother liquor containing besides all the R. mannonate of strychnine about a third of the L. salt. In order to obtain the R. acid pure, the strychnine is removed from the mixed salts left by the last experiment, and the solution of the mixed acids treated with morphine. From this liquid there separates after long standing crystals in large quantity of R. mannonate of morphine. These on purification and removal of the morphine yield R. mannonic acid, agreeing in every particular with the acid obtained from ordinary mannitol. From this acid can obviously be produced all the members of the R. series.

Here then the synthesis of the whole group from formaldehyde is complete, and as this body can be made from methylic alcohol, and the alcohol in its turn be built up from the elements, the synthesis of the whole mannitol group from the elements follows as a natural consequence. The series of reactions involved in this process are grouped in the accompanying table. The way is long and tedious at present, and the percentages of the compound formed in some of the processes very small, but no doubt better and simpler modifications will be discovered hereafter.

From Acrolein Bromide, Glycerose, or Formaldehyde arises,





I may mention in passing that Fischer found that by boiling ivory-nuts having with dilute  $\text{H}_2\text{SO}_4$ , they yield about 30 per cent. of R. mannose, and as this ferments readily, he suggests these, which are, at the present time, a waste article, as a source of alcohol.

So far nothing has been said about glucose. This body is much akin to mannose. It possesses the same structural formula, forms with phenyl-hydrazine the same glucosazone, which yields the same osone and levulose. Upon reduction, both aldehydes yield the same alcohol mannitol. Their polarising activities are, however, different. Dextrose turns much further to the right than mannose. The hydrazones are also different; that of the former being soluble, that of the latter being comparatively insoluble. By oxidation with Br both yield acids and corresponding salts. Gluconic acid forms with calcium a salt which separates from a concentrated solution in fine needles, which gradually grow in the fluid into cauliflower-shaped aggregates. This form is characteristic for gluconate of calcium.

It is evident the difference between glucose and mannose must be one of physical isomerism; and for an explanation of this we must turn to the Le Bel and Van't Hoff theory. We know that if a C atom becomes associated with four different groups, it

becomes optically active. Thus the molecules  $\begin{array}{ccc} \text{H} & \text{H} & \text{CH}_3 \\ \text{HCH} & \text{HCH} & \text{HCH} \end{array}$ , that is, methane,

methylic alcohol, ethylic alcohol, are all optically inactive; but so soon as we introduce a fourth group, and cause the C atom to be united with four different groups, we get an opti-

cally active molecule, as in lactic acid  $\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ \text{H-C-COOH} & & \text{COOH-C-H} \\ \text{OH} & & \text{OH} \end{array}$ . This can be also written

and as the groups are arranged in the one way or the other, so the acid polarises to the right or the left. Such a C atom surrounded by four different groups is called asymmetric. Though the arrangement of lactic acid can be shown on a level surface, some other peculiarities of the grouping round the C atom cannot be so exhibited; for instance, if the four bonds of the C atom were all in the same plane, there ought to be

$$\begin{array}{cc} \text{Cl} & \text{Cl} \\ \text{HCH} & \text{HCCl} \end{array}$$

two different dichloro-methanes, HCH and HCCl, which we know there are not. But

if, as according to the above-mentioned theory, the four bonds of the C atom are so arranged that if the atom be placed in the centre of a regular tetrahedron, they point to the four angles of the figure, it will be easily seen that the two Cl atoms in the before-mentioned compound, in whatever position they may be placed, invariably hold the same relation to the C nucleus.

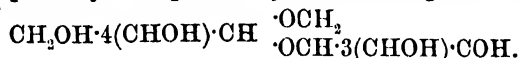
In the hexahydric aldehydes mannose and glucose, we have obviously four asymmetric C atoms, which may be designated  $\text{CHO} \cdot \underset{\text{As 1,}}{\text{CHOH}} \cdot \underset{\text{As 2,}}{\text{CHOH}} \cdot \underset{\text{As 3,}}{\text{CHOH}} \cdot \underset{\text{As 4,}}{\text{CHOH}} \cdot \text{CH}_2\text{OH}$ , and as each of these asymmetric atoms may in its turn polarise right or left—in other words, be positive or negative—sixteen modifications are possible. Fischer comes to the conclusion, on very plausible grounds, that the difference in the optical activity of mannose and glucose is caused by an alteration in the properties of the C atom marked As 1, the other three asymmetric atoms preserving the same respective relations in the two compounds; so glucose may be looked upon as the right and mannose as the left modification of the same system.

For the purpose of obtaining the gluconic series from the mannonic, the acid seemed the most suitable member to work upon. Mannonic acid may be related to gluconic either as racemic to one of the optically active tartaric acids, or as racemic to meso-tartaric acid. In the first case it should be possible to split up mannonic acid into gluconic and a second isomeride. In the second case there would be more prospect of effecting the transformation by a high temperature. After numerous failures, the conversion was effected by heating mannonic acid with chinoline to  $140^\circ \text{C}$ ., a mixture of the two acids, mannonic and gluconic, arising, just as a mixture of racemic and meso, tartaric arises upon heating cinchonine racemate to  $170^\circ \text{C}$ . After removal of the chinoline, which was liberated by  $\text{Ba}(\text{HO})_2$ , and distilled off by steam, the two acids were separated by conversion into their brucine salts, the mannonic one being insoluble and the gluconic one soluble. After removal of brucine from the gluconate, the acid is evaporated until its lactone forms. This, by reduction with Na amalgam, yields glucose, which has the same specific rotatory power and other characteristics of the natural product. Upon similar treatment the I. and L. mannonic acids should yield an I. and an L. glucose.

Fischer has also made a series of very interesting observations on the saccharons or sugars of the  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  type, which throw considerable light on the constitution of two of them, amylose and lactose.

Upon treating milk-sugar with Ph-hydrazine and acetic acid the osazone comes down, this by treatment with HCl yields the osone. If this osone be boiled with dilute HCl, inversion takes place, and a mixture of galactose and glucosone in equal molecules arises.

If this mixture be again treated with Ph-hydrazine and acetic acid Ph-glucosazone comes down first, almost in the cold, since an osone combines more readily with this base than an aldehyde. Upon warming for some time the Ph-lactosazone comes down. This shows that the molecule of milk-sugar is built up of a molecule of glucose and one of galactose that the COH portion is only free in one group, and this the glucose one, since it is the only group modified by Ph-hydrazine in the milk-sugar molecule before inversion. The COH group of the galactose portion is evidently altered in the anhydride formation, and this change may probably be expressed by the following formula :

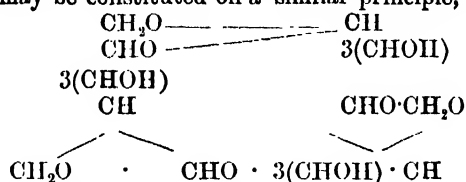


Amylon or malt-sugar upon similar treatment gives evidence of a similar anhydride formation between two molecules of glucose.

Upon treatment with Br lacton and amydon yield two acids of the composition  $\text{C}_{12}\text{H}_{22}\text{O}_{12}$ , called respectively lactobionic and maltobionic. Upon inversion lactobionic acid yields one molecule of galactose and one of gluconic acid ; maltobionic one of glucose and one of gluconic acid. This is also confirmatory of the structure given above.

The constitution of cane-sugar is still a mystery, if the attempt be made to combine, a molecule of glucose and one of levulose in a similar manner to lacton or amydon, either an aldehyde or a ketone group remains active, and this would necessarily reduce Fehling, which cane-sugar does not do. Probably the old view of its being an ether may prove to be correct.

Looking at the constitution of amydon and lacton, the idea has struck me that dextrin and starch may be constituted on a similar principle, thus,



This formula is obviously expansible into a ring of any dimensions, dextrin consisting of a smaller number of groups, starch of a much larger. Supposing such a ring of forty groups to be attacked by diastase, and broken up at one point, the ring then becomes maltodextrin, *i.e.*, a chain of dextrin groups with an amydon group at each end. The chain may then be attacked at another point and two smaller chains would arise with a higher proportion of amydon to dextrin, until at last a number of groups unite to that form of dextrin on which diastase acts with extreme difficulty.

By Killiani's cyan-hydrin process we have a method of proceeding from an aldehyde of one series to the acid of the one higher up, and in this way can be built up from the hexahydric mannose a heptahydric acid ; this can be converted into its lactone, and by reduction into the hepta-hydric aldehyde. From this, by a repetition of the process, can be formed an octohydric aldehyde, and so on. Fischer has in this manner obtained from mannose the heptahydric sugar persite. He proposes to name the aldehydes of the series similar in constitution to mannose—mannohexose, mannoheptose, etc., those akin to glucose, glucohexose, glucooctose, etc., the alcohols being expressed by changing the -ose into -itol, as mannohexitol, and the acids by changing the -ose into -onic.

On consideration of the results of these experiments, we cannot fail to be struck with some of the curious features of plant life; for instance, all the carbohydrates hitherto examined are members of the R. series; for the members of the L. we have to turn to the gums, and these are looked upon by physiologists to some extent as excretions. They also do not consist of left-handed members only, since O'Sullivan has isolated from a number of gums an arabinose which rotates powerfully to the right. Fischer is inclined to take the view that in plant life, as in artificial synthesis, the inactive series is first formed; this is then split up, the members of the R. series being used up in the formation of starch and the other carbohydrates, whilst the members of the L. serve for some other unknown purpose.

The inability of L. series to undergo alcoholic fermentation is also very curious; bacteria seem to be able to attack R. or L. equally well.

The discovery of some means of producing the levulose of the L. series (that is, the dextro-rotatory one) on a commercial scale, would be of great advantage to brewers, as it would enable them to produce a beer capable of retaining indefinitely a certain amount of sweetness, a purpose for which saccharin has been proposed. The addition of a carbohydrate sugar would be obviously much less objectionable than the use of a chemical compound, in no way allied to the sugar group except in taste.

Those desirous of pursuing the subject further are referred to the original papers in the "Berichte" of the Berlin Chemical Society, volumes xviii. to xxiii., where the fullest details will be found. Excellent abstracts have also appeared in the journal of the Chemical Society from the year 1887 up to the present time.

In conclusion, I have to thank Mr. Arthur R. Ling for much valuable assistance in the preparation of this paper.

#### ON SOME POINTS IN THE ANALYSIS OF MILK.

By H. DROOP RICHMOND

(Second Chemist in the Khedivial Laboratory, Cairo).

*Read at Meeting, June, 1890.*

THE importance of the determination of the density of milk cannot be too strictly insisted on, as it affords a most valuable means of checking the results obtained in an analysis, being, in my opinion at least, as valuable as a duplicate determination of the constituents; but there are one or two precautions to be taken in this determination other than those generally applicable to density determinations; as Vieth has recently pointed out (ANALYST, XIV., p. 69), the density of milk is not constant until about twenty-two to twenty-four hours after milking, a gradual augmentation taking place. It is the final density which should be taken as the normal density of the sample, as it is the one that has been assumed in the calculation of milk formulæ. Milk is a substance which, when shaken, holds air-bubbles very tenaciously, and sufficient time must always be given after mixing the sample to allow of the elimination of the bubbles; attention to these two points is necessary.

Some time ago I published (ANALYST, XIV., 126) a formula for calculating the fat

from the total solids and the density (a printer's error in the text gave  $T = 1.17 F - .263 \frac{G}{D}$ , the real formula being  $T = 1.17 F + .263 \frac{G}{D}$ ). This formula gave practically the same results as that published previously by Hehner and myself (ANALYST, XIII., 26), which formed the basis of the "milk scale" (ANALYST, XIII., 65). The accuracy of these formulæ for cow's milk has been corroborated by some hundreds of analyses in various laboratories in different countries.

I have now extended these formulæ to include the calculation of milk-sugar and proteids, the density, fat, total solids and ash being known.

This formula is

$$P = 2.8 T + 2.5 A - 3.33 F - .7 \frac{G}{D}$$

( $P$  = proteids ;  $T$  = total solids ;  $A$  = ash ;  $F$  = fat ;  $D$  = density ; water at  $60^{\circ}$  F. being taken as 1 ; and  $G$  =  $1000 D - 1000$ ).

The difference between the total solids and the fat, proteids, and ash gives the milk-sugar ; in this formula it has been assumed that every thing that is not fat, proteids, or ash is milk-sugar, an assumption which is not strictly correct, but which introduces a small error. Another error is probably introduced by the fact that the ash in milk is not the same as the salts existing in milk, but of this I shall speak later ; the errors between the proteids and milk-sugar found and calculated vary between  $+ .4$  and  $- .4$ .

From the formula it is easy to calculate the influence of one gram. of each of the constituents in 100 c.c. on the density and from that the density in solution.

The figures are

|          |    |    | Influence of 1 gram. in 100 c.c. |    |    | Density. |
|----------|----|----|----------------------------------|----|----|----------|
| Fat      | .. | .. | .76                              | .. | .. | .929     |
| Sugar    | .. | .. | 4.00                             | .. | .. | 1.667    |
| Proteids | .. | .. | 2.57                             | .. | .. | 1.346    |
| Ash      | .. | .. | 7.57                             | .. | .. | 4.12     |

The figures for the density show a remarkable agreement with those directly determined thus. Prof. Fleischmann has found (*J. f. Landw.*, xxxiii, 251) that the average density of butter-fat is .93 ; for milk-sugar many observers agree in giving 1.65 ; for casein Hehner (ANALYST, VIII., 253) gives 1.31, a number obtained from casein admittedly not in a state of absolute purity, while from the figures of Dupré (ANALYST, VIII., 248) I calculate that the density of casein and albumin is 1.34 ; for the ash I calculate from Dupré's figures (*loc. cit.*) a density of 3.0.

The figures are then thus :—

|            |    |    | Density in solution. |             |
|------------|----|----|----------------------|-------------|
|            |    |    | Found.               | Calculated. |
| Fat        | .. | .. | .93                  | .929        |
| Milk-sugar | .. | .. | 1.65                 | 1.667       |
| Proteids   | .. | .. | 1.31 (Hehner)        | } 1.346     |
|            |    |    | 1.34 (Dupré)         |             |
| Ash        | .. | .. | 3.0                  | 4.12        |

The agreement between the two series of figures is sufficiently exact except in the case of the ash. To this I do not attach much importance for two reasons. It is the figure on which I place least reliance, as a small variation in the factor produces a large



variation in the density calculated therefrom, being more than ten times as large as in the other constituents. Then, as Söldner has pointed out (*Landw. Versuch. Stat.* 35, 351), the ash of milk does not accurately represent the salts already existing therein, the citrates and other organic salts being decomposed into carbonates, which are neutralised by phosphoric acid produced by the combustion of the phosphorus of the casein. Neglecting the case of the ash, then, I think there is sufficient proof in the above figures that the density of milk is a simple function of that of its constituents.

The agreement between the two sets of figures also tends to show the accuracy of the methods of analysis. This is especially important in the case of the fat, as doubt has been cast on the method employed (the Adams method as modified by myself); but when we have a formula calculated actually from the results of analysis with almost identical factors to those determined directly, I maintain that it is very strong evidence that the methods employed in the analysis have been correct ones; and the formula is not one for a particular process, but becomes an absolute one.

*(Conclusion of the Society's Proceedings)*

## ON THE QUANTITY OF VOLATILE ACIDS PRESENT IN BUTTER FAT.

BY DR. P. VIETH.\*

At the meeting held in June, 1889, I laid before our Society the results of a rather extensive series of determinations of the volatile acids obtained from butter fats, treated according to Reichert-Wollny's method (*THE ANALYST*, 1889, vol. xiv., p. 147). The present paper is a continuation of that read last year. Some of the results published at that time being rather remarkable, I thought it desirable to extend the investigation and thereby collect more evidence. Last year's paper recorded results up to the 11th of June, and I will now, without further preliminaries, proceed to put before you the results obtained since then until the end of June of the present year.

A sample of pure butter-fat received from Kiel in July, 1888, which on former occasions had required from 31·6 to 32·1 c.c. deci-normal alkali, was repeatedly re-examined, with the following results:

|        |                      |              |      |
|--------|----------------------|--------------|------|
| No. 1. | Butter-fat from Kiel | (a) 19-9-89  | 31·8 |
|        |                      | (b) 12-12-89 | 32·2 |
|        |                      | (c) 15-4-90  | 32·0 |

This butter-fat has been kept in a well-stoppered bottle protected against the action of light, and does not exhibit signs of decomposition.

I had occasion to examine a large number of samples of butter, as it appears in the market; they are here arranged according to the sources from which they were derived.

### BUTTER MANUFACTURED IN LONDON.

| No. | Date.   |      | No. | Date.    |      | No. | Date.   |      |
|-----|---------|------|-----|----------|------|-----|---------|------|
| 2.  | 30-7-89 | 27·1 | 12. | 24-9-89  | 25·8 | 21. | 8-4-90  | 29·6 |
| 3.  | 6-8-89  | 26·0 | 13. | 1-10-89  | 26·1 | 22. | 15-4-90 | 28·5 |
| 4.  | 6-8-89  | 25·9 | 14. | 8-10-89  | 26·1 | 23. | 22-4-90 | 27·7 |
| 5.  | 13-8-89 | 26·2 | 15. | 15-10-89 | 26·7 | 24. | 29-4-90 | 28·3 |
| 6.  | 20-8-89 | 26·5 | 16. | 5-11-89  | 26·8 | 25. | 6-5-90  | 29·0 |
| 7.  | 20-8-89 | 26·7 | 17. | 12-11-89 | 26·8 | 26. | 13-5-90 | 28·8 |
| 8.  | 27-8-89 | 26·8 | 18. | 25-3-90  | 30·0 | 27. | 20-5-90 | 28·4 |
| 9.  | 3-9-89  | 26·3 | 19. | 25-3-90  | 29·1 | 28. | 3-6-90  | 28·6 |
| 10. | 10-9-89 | 26·0 | 20. | 31-3-90  | 29·1 | 29. | 24-6-90 | 27·2 |
| 11. | 17-9-89 | 26·4 |     |          |      |     |         |      |

\* This paper was intended for the country-meeting, which was abandoned. —P. V

All these results fall within the limits which we are accustomed to look at as normal, viz., from 25 to 30 ; they are lower in the second half of last, and higher in the first half of the present year.

## OTHER ENGLISH BUTTER.

| No. | Date.   |      | No. | Date.   |      |
|-----|---------|------|-----|---------|------|
| 30. | 15.4-90 | 27.3 | 31. | 30.5-90 | 25.0 |

Sample No. 31 was butter from a small private dairy, and very rancid when received.

## FRENCH BUTTER.

| No. | Date.    |      | No. | Date.    |      | No. | Date.   |      |
|-----|----------|------|-----|----------|------|-----|---------|------|
| 32. | 18-6-89  | 29.9 | 45. | 10-12-89 | 27.7 | 58. | 31-3-90 | 28.7 |
| 33. | 25-6-89  | 30.4 | 46. | 17-12-89 | 26.9 | 59. | 8-4-90  | 29.0 |
| 34. | 2-7-89   | 30.5 | 47. | 31-12-89 | 28.0 | 60. | 22-4-90 | 28.8 |
| 35. | 9-7-89   | 29.8 | 48. | 7-1-90   | 28.0 | 61. | 29-4-90 | 29.7 |
| 36. | 16-7-89  | 30.3 | 49. | 14-1-90  | 27.5 | 62. | 6-5-90  | 30.0 |
| 37. | 23-7-89  | 30.3 | 50. | 21-1-90  | 27.5 | 63. | 13-5-90 | 30.5 |
| 38. | 15-10-89 | 29.0 | 51. | 28-1-90  | 28.0 | 64. | 20-5-90 | 30.8 |
| 39. | 22-10-89 | 29.3 | 52. | 4-2-90   | 27.7 | 65. | 24-5-90 | 30.5 |
| 40. | 29-10-99 | 28.6 | 53. | 11-2-90  | 28.7 | 66. | 3-6-90  | 30.2 |
| 41. | 12-11-89 | 28.8 | 54. | 18-2-90  | 28.7 | 67. | 12-6-90 | 30.6 |
| 42. | 19-11-89 | 27.3 | 55. | 25-2-90  | 29.1 | 68. | 17-6-90 | 29.8 |
| 43. | 26-11-89 | 28.3 | 56. | 4-3-90   | 29.1 | 69. | 24-6-90 | 29.4 |
| 44. | 3-12-19  | 28.2 | 57. | 11-3-90  | 29.1 |     |         |      |

All these samples contained, as may be seen from the figures, rather large amounts of volatile acids, the results being, with one exception—sample No. 46—all above 27. Much has been said of late of the wholesale adulteration of butter going on in the north of France. Here we have a number of samples which were, no doubt, quite genuine and, I may add, very good in every respect.

## DANISH BUTTER.

| No. | Date.    |      | No. | Date.    |      | No. | Date.   |      |
|-----|----------|------|-----|----------|------|-----|---------|------|
| 70. | 22-11-89 | 29.8 | 71. | 27-11-89 | 28.8 | 72. | 26-6-90 | 29.9 |

The results of the examination of these few samples call for no comment.

## KIEL BUTTER.

| No. | Date.    |      | No. | Date.    |      | No. | Date.   |      |
|-----|----------|------|-----|----------|------|-----|---------|------|
| 73. | 18-6-89  | 28.6 | 82. | 22-10-89 | 21.7 | 91. | 11-2-90 | 29.8 |
| 74. | 25-6-89  | 27.6 | 83. | 29-10-89 | 22.6 | 92. | 19-2-90 | 29.7 |
| 75. | 2-7-89   | 25.9 | 84. | 5-11-89  | 21.1 | 93. | 25-2-90 | 30.2 |
| 76. | 9-7-89   | 26.7 | 85. | 4-12-89  | 29.2 | 94. | 4-3-90  | 30.7 |
| 77. | 16-7-89  | 27.5 | 86. | 10-12-89 | 29.3 | 95. | 12-3-90 | 30.2 |
| 78. | 23-7-89  | 24.7 | 87. | 17-12-89 | 29.8 | 96. | 24-5-90 | 28.9 |
| 79. | 30-7-89  | 27.6 | 88. | 22-1-90  | 30.2 | 97. | 12-6-90 | 29.4 |
| 80. | 6-8-89   | 24.2 | 89. | 28-1-90  | 29.5 | 98. | 17-6-90 | 29.9 |
| 81. | 15-10-89 | 22.8 | 90. | 4-2-90   | 29.7 |     |         |      |

The series of samples of Kiel butter comprises some with very low volatile acids. These low results have already been mentioned in a paper which I read before our Society at the February meeting of the present year (*THE ANALYST*, 1890, vol. xv., p. 44). Great doubts were then expressed as to the genuineness and purity of the samples in question, to which, of course, I cannot swear. But I repeat, most emphatically, my firmest conviction that the samples were entirely free from any sophistication whatever, coming, as they did, from two very well-known and managed dairies, which are entirely beyond suspicion. It is, perhaps, more convincing than my belief to show the peculiar variations which the amounts of volatile acids underwent.

From the one dairy samples were examined at the following dates and with the following results:—

|                           |          |      |
|---------------------------|----------|------|
| No. 55, last year's paper | 28-5-89  | 27.3 |
| " 56 " " "                | 4-6-89   | 28.7 |
| " 57 " " "                | 11-6-89  | 27.4 |
| " 74 present paper        | 25-6-89  | 27.6 |
| " 75 " "                  | 2-7-89   | 25.9 |
| " 78 " "                  | 23-7-89  | 24.7 |
| " 80 " "                  | 6-8-89   | 24.2 |
| " 81 " "                  | 15-10-89 | 22.8 |
| " 84 " "                  | 5-11-89  | 21.1 |
| " 85 " "                  | 4-12-89  | 29.2 |
| " 86 " "                  | 10-12-89 | 29.3 |

From the other dairy the following results were obtained:—

|                      |          |      |
|----------------------|----------|------|
| No. 76 present paper | 7-7-89   | 26.7 |
| " 77 " "             | 16-7-89  | 27.5 |
| " 79 " "             | 30-7-89  | 27.6 |
| " 82 " "             | 22-10-89 | 21.7 |
| " 83 " "             | 29-10-89 | 22.6 |
| " 88 " "             | 22-1-90  | 30.2 |
| " 90 " "             | 4-2-90   | 29.7 |
| " 91 " "             | 11-2-90  | 29.8 |
| " 92 " "             | 19-2-90  | 29.7 |
| " 93 " "             | 25-2-90  | 30.2 |
| " 94 " "             | 4-30-90  | 30.7 |
| " 96 " "             | 24-5-90  | 28.9 |

In the case of both dairies, but more notably in the case of the first one, where there are not so large intervals between the several samples, we notice the volatile acids to drop down to an exceedingly low point during the time from August to November. This is the time when, in Schleswig-Holstein, most of the cows are at the end of the period of lactation. That the butter-fat present in the milk of stale cows contains, as a rule, an amount of volatile acids below the normal limit has been found by several observers, and this fact has certainly something to do with the low results in question. I am, however, inclined to think that there were other natural influences at work, and am glad to know that the matter will be closely investigated this year under more favourable conditions than those under which I had to work.

Investigations executed in various countries have proved beyond doubt that the volatile acids in butter-fat fall below the normal limit much more frequently than was supposed to be the case about two years ago. The fact exists, but as to the reasons we are still very much in the dark. I shall have to add a further number of abnormal cases, but as to their explanation, I am afraid I have nothing to advance.

The samples which I have to mention in what follows are all samples of butter produced in my laboratory by shaking cream in a wide-mouthed, glass-stoppered bottle.

Two samples of cream received from a butter-factory in Sussex gave the following results:—

#### CREAM FROM GL., SUSSEX.

| No. | Date.   |      | No.  | Date.         |
|-----|---------|------|------|---------------|
| 99. | 24-6-89 | 28.5 | 100. | 10-12-89 28.6 |

I am now coming to a series of samples comprising abnormal results. The butter-fat to which all these samples refer was obtained from cream, separated by centrifugal force from the milk yielded by cows, which were kept at the Aylsbury Dairy Company's estate near Horsham.

I had found last year that the volatile acids in butter-fat produced by the cows kept on the said estate, were abnormally low during the month of February, March, and part of April; that the results rose up to and above the limit of 25 towards the end of April, and that they kept so, though never rising very high, until the early part of June. Since then the following results have been obtained:--

## CREAM FROM HORSHAM.

| No.  | Date.    |      | No.  | Date.    |      | No.  | Date.   |      |
|------|----------|------|------|----------|------|------|---------|------|
| 101. | 18-6-89  | 26.2 | 120. | 28-10-89 | 25.4 | 138. | 3-3-90  | 24.1 |
| 102. | 24-6-89  | 26.2 | 121. | 4-11-89  | 24.8 | 139. | 10-3-90 | 23.3 |
| 103. | 1-7-89   | 25.5 | 122. | 11-11-89 | 24.8 | 140. | 17-3-90 | 23.8 |
| 104. | 9-7-89   | 25.9 | 123. | 18-11-89 | 25.1 | 141. | 24-3-90 | 23.6 |
| 105. | 16-7-89  | 25.8 | 124. | 25-11-89 | 24.0 | 142. | 31-3-90 | 23.6 |
| 106. | 23-7-89  | 25.7 | 125. | 2-12-89  | 23.9 | 143. | 7-4-90  | 24.3 |
| 107. | 29-7-89  | 26.1 | 126. | 10-12-89 | 21.7 | 144. | 14-4-90 | 24.5 |
| 108. | 5-8-89   | 25.8 | 127. | 16-12-89 | 22.6 | 145. | 21-4-90 | 25.6 |
| 109. | 12-8-89  | 25.1 | 128. | 23-12-89 | 21.3 | 146. | 28-4-90 | 25.7 |
| 110. | 19-8-89  | 24.9 | 129. | 30-12-89 | 21.7 | 147. | 5-5-90  | 25.1 |
| 111. | 27-8-89  | 25.1 | 130. | 6-1-90   | 22.1 | 148. | 12-5-90 | 25.9 |
| 112. | 3-9-89   | 23.7 | 131. | 13-1-90  | 23.1 | 149. | 19-5-90 | 25.4 |
| 113. | 10-9-89  | 23.9 | 132. | 20-1-90  | 23.3 | 150. | 24-5-90 | 25.0 |
| 114. | 16-9-89  | 23.3 | 133. | 27-1-90  | 23.2 | 151. | 2-6-90  | 25.6 |
| 115. | 24-9-89  | 23.3 | 134. | 3-2-90   | 23.1 | 152. | 9-6-90  | 26.2 |
| 116. | 30-9-89  | 23.8 | 135. | 10-2-90  | 22.6 | 153. | 17-6-90 | 25.8 |
| 117. | 7-10-89  | 24.2 | 136. | 17-2-90  | 23.9 | 154. | 24-6-90 | 25.0 |
| 118. | 14-10-89 | 25.2 | 137. | 24-2-90  | 23.6 | 155. | 30-6-90 | 25.6 |
| 119. | 21-10-89 | 25.8 |      |          |      |      |         |      |

The figures show that the results kept above 25 until the end of August; that they dropped below 25 during September and part of October; that they rose again and kept above, or almost up to 25 till about the middle of December; that they were below 25 from that time until the middle of April; and, lastly, that from the second half of April up to the time at which the present record closes, they were again, slightly though, but regularly above 25. On comparing the results of last and the present year, so far as that is possible, one finds that the figures present similar features in their fluctuations.

As to the herd of cows yielding in their milk a fat of so frequently abnormal composition, it was, in June, 1889, composed of Shorthorn, Jersey and Kerry cows. The Jerseys were eliminated in the latter part of August, 1889, and since that time there were about fifty cows milked daily, about three-fourths of that number being Shorthorns and one-fourth Kerrys. The cows are kept in exceptionally well built, lighted and ventilated sheds, which some of our members will, I dare say, remember, from the visit which our Society paid to the estate in June, 1887. The cows do not calve at one particular time of year; care is, moreover, taken that there are always cows in the

various stages of lactation. The food is, for the most part, home-grown, and does not present any unusual features, as, indeed, do none of the conditions under which the cows are kept.

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#### SOME POINTS IN THE DETERMINATION OF SILICA IN SILICATES BY FUSION WITH ALKALINE CARBONATES.

By JAMES P. GILBERT, S.B.

THE usual method of determining silica in silicates—that of fusion with the alkaline carbonates, decomposition with hydrochloric acid, and subsequent evaporation to dryness—does not always give satisfactory results. This method is universally described in the text-books as being accurate, with the occasional caution that the filtrate should also be examined for any silica which may not have been rendered insoluble by evaporation to dryness. But one looks in vain for any intimation of what may be the amount of the error, in the determination of silica as usually carried out, if one neglects to examine the filtrate. There is no doubt that many chemists have had trouble with this method, and some have given it up, preferring to volatilize the silica with hydrofluoric and sulphuric acids, and after a careful analysis of the residue, to calculate the silica by difference. A recent writer\* makes the statement that he has never been able to obtain more than 97.5 per cent. of the total silica in highly siliceous bodies by the fusion method. The following work was undertaken in the hope of discovering some of the sources of error in the fusion process.

The influence of the temperature at which the silica is dehydrated was first investigated. Most authorities say that evaporation on the water bath to complete dryness, or until no more hydrochloric acid is given off, is sufficient to dehydrate the silica, but a few recommend subsequent heating in an air-chamber to a temperature of 110° C. A higher temperature than 110° C. is said by Fresenius to be inadmissible, since there is liability of the silica recombining with the bases present to form silicates partially decomposable with hydrochloric acid.

To test the influence of temperature on the amount of silica obtained, the following determinations of silica were made in a blast-furnace slag containing about 46 per cent. of lime, 10 per cent. of alumina, and less than one per cent. of magnesia. The silica was dehydrated at various temperatures, but in all other respects the process was carried out exactly as Fresenius directs. What is generally called silica, that is, the mass insoluble in hot hydrochloric acid after evaporation to dryness, is given in Column I. of the following table. This was treated with hydrofluoric acid, and the weight of the residue is given in Column II. In the filtrate from the silica, the alumina was precipitated by ammonia, dried, ignited, and then fused with potassium bisulphate. The residue left on treating the fused mass with water (and correcting for the impurities of the bisulphate used) is given in Column III. The total silica in Column IV. is calculated by subtracting the weight of the residue left after treatment with hydrofluoric acid from the weight of the silica as given in Column I., and adding that found with the alumina in Column III.

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\* George Craig: *Chem. News*, Vol LX., No. 1563.

TABLE I.—ANALYSES OF BLAST-FURNACE SLAG (CONTAINING 46 PER CENT. LIME) BY FUSION WITH ALKALINE CARBONATES.

|    | I.<br>Residue insoluble in<br>hydrochloric acid<br>after evaporation<br>to dryness. | II.<br>Weight of residue<br>obtained from treat-<br>ing Column I. with<br>hydrofluoric acid. | III.<br>Weight of Silica<br>found in Alumina. | IV.<br>Total Sil'ca. |
|----|---|--|---|----------------------|
|    | Per cent.   | Grams.   | Grams.  | Per cent.            |
| 1  | 41.25   | .0003  | .0006   | 41.26                |
| 2  | 41.34   | .0024  | .0008   | 41.17                |
| 3  | 41.39   | .0012  | .0009   | 41.33                |
| 4  | 41.32   | .0020  | .0003   | 41.18                |
| 5  | 41.22   | .0012  | .0009   | 41.19                |
| 6  | 41.43   | .0021  | .0007   | 41.23                |
| 7  | 41.40   | .0014  | .0009   | 41.32                |
| 8  | 41.48   | .0017  | .0008   | 41.35                |
| 9  | 41.33   | .0013  | .0005   | 41.25                |
| 10 | 41.71   | .0036  | .0007   | 41.42                |
| 11 | 41.53   | .0028  | .0007   | 41.27                |
| 12 | 41.89   | .0031  | .0004   | 41.35                |
| 13 | 41.79   | .0032  | .0002   | 41.41                |
| 14 | 41.65   | .0027  | .0005   | 41.43                |
| 15 | 41.90   | .0028  | .0001   | 41.48                |

Nos. 1 to 3 inclusive were dehydrated on the water bath.

Nos. 4 to 6 inclusive were dehydrated at 125° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate over Bunsen burner.

Nos. 10 to 15 inclusive were dehydrated in air-chamber at 280° C.

All evaporations were made in porcelain.

In this series of results it will be seen that the silica was practically all rendered insoluble, even at the temperature of the water bath, and that there was no gain in this respect in using a higher temperature. But the amount of foreign matter in the silica was, in general, perceptibly higher at the higher temperature of dehydration. This is probably due to the alumina being rendered partially insoluble in acid. From the fact that very little silica was found in the alumina, it would seem as if there were no tendency for the silica to recombine with the lime and alumina even at a temperature of 280° C. Nos. 13, 14, and 15 were digested, after dehydration, with hot acid for one hour, in the expectation of dissolving out all the alumina and other bases, but this treatment did not give smaller residues, after the volatilization of the silica with hydrofluoric acid, than in Nos. 10, 11, and 12, which were treated only thirty minutes with acid.

The general uniformity of the results in this series suggested the possible influence of the calcium chloride present in dehydrating the silica on evaporation to dryness. This led to the second point considered, namely, the influence of the salts

present on the determination of silica. It is not unreasonable to suppose that some salts, such as calcium chloride, may have a beneficial influence, while others, as, for example, magnesium chloride, which is decomposed when its solution is evaporated, may vitiate the silica determination by forming a silicate which will be subsequently decomposed by hydrochloric acid with solution of the silica. To test the effect of magnesium chloride, determinations of silica were made in a slag containing about 35 per cent. of lime, 15 per cent. of magnesia, and 15 per cent. of alumina. (See Table II.)

TABLE II.—ANALYSES OF A BLAST-FURNACE SLAG (CONTAINING 35 PER CENT. LIME AND 15 PER CENT. MAGNESIA).

|    | I.<br>Residue insoluble in<br>hydrochloric acid<br>after evaporation<br>to dryness. | II.<br>Weight of residue<br>obtained from treat-<br>ing Column I. with<br>hydrofluoric acid. | III.<br>Weight of Silica<br>found in Alumina. | IV.<br>Total Silica. |
|----|---|--|---|----------------------|
|    | Per cent.   | Grams.   | Grams   | Per cent.            |
| 1  | 33·65   | ·0032  | ·0032   | 33·61                |
| 2  | 32·90   | ·0014  | ·0025   | 33·18                |
| 3  | 33·46   | ·0013  | ·0013   | 33·29                |
| 4  | 33·71   | ·0027  | ·0004   | 33·40                |
| 5  | 33·42   | ·0021  | ·0008   | 33·24                |
| 6  | 33·75   | ·0031  | ·0004   | 33·36                |
| 7  | 33·49   | ·0032  | ·0011   | 33·24                |
| 8  | 33·85   | ·0045  | ·0012   | 33·27                |
| 9  | 33·90   | ·0042  | ·0012   | 33·30                |
| 10 | 33·65   | ·0062  | ·0062   | 33·62                |
| 11 | 33·83   | ·0046  | ·0045   | 33·80                |
| 12 | 33·95   | ·0088  | ·0050   | 33·60                |

Nos. 1 to 3 inclusive were dehydrated on the water bath.

Nos. 4 to 6 inclusive were dehydrated at 120° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate over Bunsen burner.

Nos. 10 to 12 inclusive were dehydrated at 280° C.

This series differs from the first mainly in the large amount of impurity in the silica and the large amount of silica in the alumina when the dehydration is effected at a temperature of 280° C. The best results were obtained at a temperature of 120° C. The increase of silica in the alumina as the temperature is increased would seem to be due to the magnesia, for the conditions were, in all other respects, the same as in the analyses of the other slag. The above results indicate that there is no danger of the silica combining with the magnesia at 120° C., and that at this temperature the silica is almost completely dehydrated, the calcium chloride probably assisting in the dehydration.

A series of analyses was next made on orthoclase, practically free from lime and magnesia.

TABLE III.—ANALYSES OF A SAMPLE OF ORTHOCLASE.

|   | I.<br>Residue insoluble in<br>hydrochloric acid<br>after evaporation<br>to dryness. | II.<br>Weight of residue<br>obtained from treat-<br>ing Column I. with<br>hydrofluoric acid. | III.<br>Weight of Silica<br>found in alumina. | IV.<br>Total Silica. |
|---|---|--|---|----------------------|
|   | Per cent.*  | Grams.   | Grams.  | Per cent.            |
| 1 | 64·80   | ·0018  | ·0004   | 64·52                |
| 2 | 64·13   | ·0018  | ·0030   | 64·30                |
| 3 | 64·03   | ·0026  | ·0035   | 64·20                |
| 4 | 64·35   | ·0020  | ·0030   | 64·52                |
| 5 | 64·98   | ·0050  | ·0019   | 64·45                |
| 6 | 64·62   | ·0035  | ·0020   | 64·36                |
| 7 | 64·83   | ·0068  | ·0030   | 64·45                |
| 8 | 64·97   | ·0083  | ·0039   | 64·35                |

Nos. 1 and 2 were dehydrated on the water bath.

Nos. 3 and 4 were dehydrated at 120° C.

Nos. 5 and 6 were dehydrated on iron plate over Bunsen burner.

Nos. 7 and 8 were dehydrated at 280° C.

This series differs from the previous one in that the higher temperature is not accompanied with an increased amount of silica in the filtrate. This would seem to be a confirmation of the idea that there was a recombination of the silica and the magnesia at the temperature of 280° C. in the magnesia slag; and the fact that the amounts of silica found in the alumina are (with one exception) uniformly higher than those in the lime slag indicates, I think, the beneficial effect of the calcium chloride in the dehydration of the silica.

(To be continued.)

## REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

THE IODINE NUMBER OF URINE AND ITS MEANING. A. JOLLES. (*Wr. Med. Wochenschr. Chem. Zeit.*, No. 15, 1890).—The author calls the iodine figure the quantity of iodine absorbed by 100 parts of urine solids. To carry out the analysis, 10 c.c. of the filtered urine are put into a glass-stoppered bottle, holding about 100 c.c., and mixed with 4 c.c. or more  $\frac{n}{10}$  iodine. After standing in the dark for eighteen hours, the liquid is titrated in the usual manner with  $\frac{n}{10}$  hypo, adding starch solution at once if the urine was dark-coloured. Care must be taken there is a decent excess of iodine left. The amount of solid matter per litre may be calculated from the formula  $T = (s-1) 2330$   $s$  representing the specific gravity. If 10 c.c. of urine absorb  $j$  grammes of iodine, the iodine figure of the sample  $= \frac{10000j}{(s-1)2330} = \frac{j}{s-1} 4.292$ .



The following constituents of urine absorb iodine : uric acid, urobilin, and bodies belonging to the phenol type. From the investigation of about 140 healthy urines, the author puts down the iodine figure from 4 to 5.5. The variation chiefly depends on the amount of uric acid.

If the urine is from an unhealthy person, and contains an excess of bilious acids and colouring matters, the iodine figure is much increased, and may come as high as 15. Albumenoids do not absorb any iodine, but in presence of pus the urine will give a very high iodine absorption. It therefore seems the process may prove a valuable addition to the analysis of urine.

L. DE K.

THE KJELDAHL-GUNNING PROCESS FOR ESTIMATING NITROGEN. A. ATTERBERG (*Chem. Zeit.*, No. 31, 1890).—The author strongly recommends this process, a full description of which will be found in the ANALYST, 1889. Even such bodies as quinine and indigotine practically yield all their nitrogen as ammonia. This is no matter of surprise, as in this process the sulphuric acid, instead of getting weaker on boiling, actually gets stronger. No additions of potassium permanganate or mercury, phosphoric anhydride, or scores of other bodies are required ; also no potassium sulphide during the distillation.

The author hopes this process will be soon universally adopted in agricultural laboratories.\*

L. DE K.

SIMPLE PROCESS FOR THE ESTIMATION OF NITROGEN IN CHILI-SALTPETRE. O. FOERSTER (*Chem. Zeit.*, No. 31, 1890).—When nitrates are repeatedly evaporated with hydrochloric acid, they are gradually converted into chlorides. On this fact the author has founded a process for the assay of nitrate, which, on account of its simplicity and cheapness, will no doubt be adopted. From 2 to 3 grammes of the sample are weighed out (or an aliquot part of the watery solution is pipetted off) and heated to fusion in a weighed porcelain crucible with lid. After cooling and weighing, 25 c.c. of hydrochloric acid (3 volumes of acid, 1 volume of water) are introduced, and the whole evaporated to dryness. This treatment with acid is then repeated twice to expel all nitric acid. The hydrochloric acid must not be too concentrated, otherwise there would be effervescence and spurting. The residue is finally heated for some time to 150° C., then heated to dull redness, and finally weighed. The amount of nitrogen is now calculated as follows : Instead of the molecule  $\text{NO}_3$ , there comes one atom of chlorine. Therefore the loss in weight is in respect to the nitrogen, as the difference between the molecular weight of  $\text{NO}_3$  and the atomic weight of the chlorine to the atomic weight of the nitrogen ; therefore, as  $61.89 - 35.32 = 26.57 : 14.01$ , or as  $1 : 1.896$ .† The amount of nitrogen is therefore ascertained by multiplying the loss in weight by this factor. It is a pity this process cannot be applied when the sample contains magnesium chloride, as this substance loses hydrochloric acid on drying. The test-analyses are very satisfactory.

L. DE K.

Note by abstractor.—Gunning even succeeded in completely oxidising as much as 100 grammes of meat by his process. Liquids are first evaporated to nearly dryness.—L. de K.

† "Revised Atomic Weights," L. Meyer and K. Seubert.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSIS.

### NOTE ON THE DETECTION OF HOP SUBSTITUTES IN BEER.

By A. H. ALLEN AND W. CHATTAWAY.

*Read at Meeting, June 1890.*

THE method described by one of us in the ANALYST for June, 1887, satisfactorily distinguishes between hops and hop-substitutes in the majority of cases.

It fails sometimes to remove the whole of the natural bitter of the hop, especially in cases where the hops are old. In such cases a better result can be obtained if the excess of lead be removed by boiling with sulphuric acid, instead of by sulphuretted hydrogen, in accordance with the suggestion of Mr. Adams. Concentration in presence of the sulphuric acid appears to be preferable to mere boiling of the dilute acid solution before neutralising with chalk. If the concentrated liquid be agitated with chloroform, most of the bitter principles are extracted (with the exception of chiretin). On evaporating the chloroform solution to dryness, taking up the residue in a few drops of alcohol, adding water, and *tasting* the solution, traces of bitter principles can be detected which wholly escape recognition when the taste of the treated and concentrated beer is observed. Traces of hop-bitter are often detectable when this delicate means of observation is used. According to Dr. James Bell, the extractive matters of the beer interfere with the complete precipitation of the hop-bitter by lead acetate, though that reagent precipitates the bitter principles perfectly from a simple aqueous infusion of hops. Dr. Bell finds that the solvent power of ether on quassia bitter is very limited, while the hop-bitters are readily extracted. Hence on concentrating beer and shaking the acidulated liquid three or four times with ether the whole of the hop-bitter is extracted,

while a large portion of the quassia bitter remains in the aqueous liquid and can be extracted with chloroform. If the ethereal solution be evaporated and the residue dissolved and treated with lead acetate, Dr. Bell finds the hop-bitter to be entirely precipitated, while the quassia bitter remains in solution.

We are able confirm Dr. Bell's experience to some extent. That is, we find that if a beer bittered with old hops be clarified by lead acetate, the filtrate extracted by chloroform or ether, and the aqueous solution of the more or less bitter chloroform or ether residue again treated with lead acetate, the remaining hop-bitter is in most cases entirely precipitated; though in the case of one obstinate sample of old hops sent us by Mr. Adams the bitter was not wholly removed even by this supplementary treatment. Our experience is not in accordance with Dr. Bell's so far as the behaviour of quassia with ether is concerned, the bitter being far too easily extracted by ether to render that solvent available as a means of separating quassia and hop-bitters.

With regard to the modified method (Process II.), submitted by the President at the May meeting of the Society, a few experiments made by us have given very satisfactory results. Thus an obstinate sample of old hops, the bitter of which could not be removed by more simple treatment, gave a perfectly satisfactory result when previously treated with baryta-water as recommended by Mr. Adams.

But the advantage gained by a more perfect precipitation of the hop-bitter will be more than counterbalanced if the treatment pursued resulted in the destruction of any of the bitters of the hop-substitutes; and fearing that this might be the case, in our recent experiments we have rather adopted the opposite plan. By so doing, lead precipitation is still relied on as a sorting test, but in the event of a bitter being present which resists the treatment, we prefer to ascertain its nature more fully. This can be done by using the sorting action of chloroform and ether as solvents, and treating the extracts obtained by the evaporation of these with ammoniacal basic lead acetate. This reagent precipitates the bitter principles of old hops and gentian, while leaving those of quassia, calumba, and chiretta in solution. The bitter principles of these substitutes can be recognised to some extent by special tests, which we hope further to amplify and improve; but already we have achieved such a degree of success as to justify us in laying certain of the results before the Society.

Our experiments were first made on decoctions of hops, quassia, chiretta, gentian, and other hop substitutes, and as these proved successful, we proceeded to try the process on mild beer, to which sufficient of the different bittering substances was added to convert it into a fairly palatable bitter beer. Our experiments are not, therefore, open to the objection raised against those of Dr. Bell and Mr. Bannister, described before the Hop Industry Committee. These chemists obtained beer and added quassia and other hop-substitutes in proportions largely in excess of those which would be used in practice, and thus operated under conditions unfairly favourable to their detection.

The following table exhibits the method we have so far found most successful for effecting the separation and detection of bitter principles in beer. By the use of other reagents, especially ferric acetate, a further differentiation can be effected, but we prefer to postpone a description of these experiments till we have verified the reactions at leisure.

## OUTLINE PROCESS FOR THE DETECTION OF BITTER PRINCIPLES IN BEER.

A. H. ALLEN AND W. CHATTAWAY.

1 litre of beer is evaporated to  $\frac{1}{2}$  and precipitated boiling with neutral lead acetate; the liquid boiled for fifteen minutes and filtered hot. If any precipitate occur on cooling, the liquid is again filtered.

|   |  |  |   |
|---|--|--|---|
| <p>PRECIPITATE contains <i>hop</i> bitter, <i>caramel</i> bitter, <i>ophelic acid</i> (from <i>chiretta</i>) phosphates, albuminous matters, etc., etc.</p> | <p>FILTRATE. The excess of lead is removed by passing sulphuretted hydrogen, and the filtered liquid concentrated to about 150 c.c. and tasted. It is then slightly acidulated with dilute sulphuric acid, and shaken repeatedly with chloroform.</p>  |  |   |
| <p>composed by sulphuretted hydrogen, and the solution agitated with chloroform.</p>  | <p>CHLOROFORM SOLUTION on evaporation leaves a bitter extract in the case of <i>gentian</i>, <i>calumba</i>, <i>quassia</i>, and <i>old hops</i> (only slightly or doubtfully bitter in the case of <i>chiretta</i>). The residue is dissolved in a little alcohol, hot water added, and the hot solution treated with ammoniacal basic lead acetate and filtered.</p> | <p>AQUEOUS LIQUID is shaken with ether.</p>  |   |
|   | <p>PRECIPITATE contains <i>old hops</i>, <i>gentian</i>, and traces of <i>caramel</i> products. It is suspended in water, decomposed by sulphuretted hydrogen, and the solution agitated with chloroform.</p>  | <p>FILTRATE is boiled to get rid of ammonia, and treated with a slight excess of sulphuric acid, filtered and tasted. If bitter, it is agitated with chloroform, and the residue examined for <i>calumba</i> and <i>quassia</i>.</p> | <p>ETHEREAL SOLUTION leaves a bitter residue in the case of <i>chiretta</i>, <i>gentian</i>, or <i>calumba</i>. It is dissolved in a little alcohol, hot water added, and the hot solution treated with ammoniacal basic lead acetate and filtered.</p>   |
| <p>CHLOROFORM SOLUTION is examined by special tests for <i>gentian</i> and <i>old hop</i> bitter.</p>   | <p>AQUEOUS SOLUTION contains traces of <i>caramel</i> bitter.</p>  | <p>PRECIPITATE is treated with water and decomposed by sulphuretted hydrogen. The filtered liquid is <i>bitter</i> in presence of <i>gentian</i>.</p>  | <p>FILTRATE is treated with a slight excess of dilute sulphuric acid, filtered and tasted. A bitter taste indicates <i>calumba</i> or <i>chiretta</i>, which may be re-extracted with ether and further examined.</p>   |
|   |  |  | <p>AQUEOUS LIQUID, if still bitter, is rendered alkaline and shaken with ether-chloroform. A bitter extract may be due to <i>Berberine</i> (<i>calumba</i>) or <i>Strychnine</i>.</p> <p>The aqueous liquid, separated from the ether-chloroform may contain <i>Caramel</i> bitter or <i>Choline</i> (somewhat bitter.)</p> |

In conclusion, we may say that the best way to taste bitter principles is to place some of the solution on the back of the tongue with the aid of a small pipette. When there is sufficient material, some of the solution may be swallowed with advantage. But the anterior parts of the tongue are far less sensitive to bitter principles than the parts towards the uvula.

(Conclusion of the Society's Proceedings.)

## DR. SYKES' PAPER ON THE SUGAR GROUP.

## CORRIGENDA AND ADDENDA.

Page 163, line 6, for  $C^{12}HN_2O_5$  read  $C_{12}H_{18}N_2O_5$ .

„ 163, line 12, for  $3C_6HN_2H_3 + C_6HO_6$  read  $3C_6H_5 \cdot N_2H_3 + C_6H_{12}O_6$ .

„ 163, line 13, for  $C_1H_{22}NO_4 + C_6H \cdot NH_3$  read  $C_{12}H_{22}N_4O_4 + C_6H_5 \cdot NH_3$ .

„ 165, line 6 from bottom, for  $CH_1O_6$  read  $C_6H_{12}O_6$ .

„ 165, line 17 from bottom, for  $+CHOH \cdot CHOH \cdot COH$  read  $+CH_2OH \cdot CHOH \cdot COH$ .

„ 167, middle of page, for  $H_2SO$  read  $H_2SO_4$ .

„ 168, line 5 from bottom for  $C_{12}H_{22}O_1$  read  $C_{12}H_{22}O_{11}$ .

SINCE the paper was written, Dr. Fischer has succeeded in producing the L and I glucoses. L gluconic acid can be obtained by heating L mannonic acid with chinoline, but the yield is small. It is much more readily obtained by hydrolising the cyanhydrin of arabinose, L gluconic acid and L mannonic acid being formed at the same time. The simultaneous formation of two stereo-isomerides by the addition of HCN to an aldehyde is remarkable, and it is the first time the phenomenon has been observed.

From manno-hexose (obtained by hydrolising ivory nut shavings) (reserve cellulose), the hepta-hydric manno-heptose, gluco-heptose and fructo-heptose have been obtained by the cyanhydrin process. From manno-heptose there have been formed manno-octose and gluco-octose, also from manno-octose manno-nonose. The most of these products exceed in beauty and ready crystallizability the derivatives of the hexose group. Another curious fact has been observed, viz., that only those groups which contain three carbon atoms, or a multiple of three, are capable of undergoing alcoholic fermentation with yeast. Thus the glucerose, hexose and nonose groups only ferment, and this explains the hitherto observed fact that arabinose (pentose) was an unfermentable body.

## NOTE ON THE MUNICIPAL LABORATORY IN AMSTERDAM.

BY L. DE KONINGH, F.C.S.

SINCE 1879 this laboratory has been managed by a staff of three public analysts (called *Inspecteurs*), one assistant analyst, and ten inspectors (*Keurmeesters*), three of whom take part in the practical analytical work. In England the analyst receives but very few samples which may be considered food proper, but in the above laboratory such foods as meat, fish, poultry, vegetables, preserves, whether in the fresh or prepared state, are occasionally examined. The authorities do not as a rule interfere with the wholesale trade, but take every possible precaution that articles sold retail shall not only be unadulterated, but in a clean state fit for consumption. The inspectors, who report directly to the analysts, and not to sanitary committees, and who are temporary inspectors of police (to enable them to legally seize goods), at once order the destruction of any article which is either damaged by water, fire, or is in a state of decomposition or rancidity. If the shopkeeper insists upon its first being shown to the analysts, of course his wish is gratified.

Eating-houses—even hotels—are occasionally invaded by the inspectors, and we must, I think, admit it would not be a bad thing for the poor if this kind of thing was done over here in some of the less aristocratic quarters.

The power of seizure and confiscation seems to frighten the shopkeepers more than a fine, and is, we believe, a more beneficial measure for the public than which happens in England. Here, for instance, a cheesemonger is prosecuted for selling margarine instead of natural butter. True, when the Court is satisfied he gets a fine heavy enough, but to compensate himself to a certain extent he goes on selling the stuff for a few days, and if he has any left it is mixed up to the extent of say 20 per cent. with pure butter, and so gradually got rid of. He does not entertain the least fear of being caught; as he knows by experience the public analyst will think twice before touching a mixture. This is not due to incompetence, but merely to the fact that if the shopkeeper is at all in a fighting mood he can engage an analyst who may perhaps hold a contrary opinion. No such nonsense in Amsterdam. True, the retailer gets his duplicate sample, but in these eleven years nobody has ever yet come to Court armed with a certificate from an analyst disputing the adulteration, simply because they know the Court is not likely to distrust the certificate of the *legally appointed authorities*.

In cases of grave dispute the case may be referred to some of the professors connected with the University, but their services have not as yet been required. If they ever should we may be sure they would do all in their power to uphold the analyst's certificate.

The appointments are permanent, not as in England yearly ones, and at fixed salaries. We fancy many a public analyst—particularly in the so-called country districts—would not mind being appointed on the same conditions. As matters stand now we know of many public analysts whose income derived from their office amounts to barely a few pounds a year. This is mostly caused by the inspector (who often seems to be the real chief) simply neglecting his duty without any fear of being called to account.

In a laboratory where the officials are possessed of so much power, it becomes doubly important no blunders shall be made; and we fancy that through their system of checking the results not much danger exists in Amsterdam. We will now give our readers a few of the processes and standards in use at that laboratory.

#### MILK.

The total solids not to be lower than 11.00; fat not less than 3. Consequently Sng 8.0. This standard may seem too low to British analysts, but analyses made by us of genuine Dutch milk by the SPA method fully confirms this standard. As a check on the analyses the specific gravity is always taken, and every sample is put to cream. To better read off the cream the milk is mixed with a drop or two of methyl-violet, which colours the whey, but does not dissolve in the cream. In regard to this important article of food we must confess we prefer the English plan of prosecuting when the milk falls decidedly below standard, never mind its price. In Amsterdam they practically allow any amount of adulteration with water if the price is in agreement with the dilution.\*

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\*The water used may have been very impure.

## BUTTERMILK.

Acidity not to exceed .3 per cent. The inspectors carry with them a bottle partially filled with a standard ammonia, and coloured with litmus. On adding a definite quantity of the sample the liquid should not turn red. If so there is excess of acid, and without further trouble the supply is at once rendered unsaleable by the addition of some strong colouring matter. Occasionally the samples are taken to the laboratory and tested for excess of salt, showing the use of brackish water.

## BUTTER, CHEESE.

Reichert's process. Standard for calculation 12.5 c.c. Every month a butter is prepared of the cream derived from the mixed milk of about 500 cows. Now, if they find this to take say, only, 11 c.c. no butter is touched that month unless it comes decidedly under 11. Water, 16 per cent. of which is allowed, is estimated in Hoorn's apparatus. A weighed portion of the butter is dissolved in benzol, when the water neatly collects in a narrow graduated tube. Salt and caseine, of which there should be no more than 4 per cent. are estimated as usual. Cheese is extracted with ether, and the fat submitted to Reichert's process.

## MEAT, SAUSAGES.

The question often arises whether meat, even if apparently still fresh, is likely to soon turn. When meat is distilled with water, the distillate of good meat should remain clear on addition of mercuric chloride. If now a decided precipitate is obtained the sample is at once condemned, and the whole supply destroyed. Hams are constantly examined for trichini, but very few bad cases occur.

## BREAD AND FLOUR.

Tested chiefly for alum. The admixture has practically ceased, only two cases having occurred last year.

## SWEETS, PRESERVES, AERATED BEVERAGES.

These are all tested for metals, a very small quantity sufficing for their seizure and destruction. One litre of soda-water should leave on evaporation a residue in which neither copper nor lead can be detected. Although some authorities hold that all these articles are much improved by a good, sound dose of copper or lead, no harm has ever come yet from the enforced supply of metal-free aerated water.

## SPIRITS, WINES, BEERS.

Spirits are tested for strength, also for fusel-oil, .2 per cent. of which is allowed.\* Should the amount be large the spirit is confiscated. We have been gravely informed some English authorities consider the presence of amylic alcohol highly beneficial; but we can assure the public the grave symptoms of alcoholism are decidedly on the decrease in Amsterdam, thanks to the action taken by the public analysts.

Whether harmless or not, neither salicylic acid nor saccharine are allowed in wines or beers.

## PEPPER.

This article when containing excess of husk or stalks is condemned. The analyses are chiefly done microscopically.

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\*Qualitatively tested for with sulphuric acid and furfural, quantitatively by R  se's chloroform process.

## SOME POINTS IN THE DETERMINATION OF SILICA IN SILICATES BY FUSION WITH ALKALINE CARBONATES.

BY JAMES P GILBERT, S.B.

*(Continued from page 179.)*

The third point considered was the influence of temperature on the dehydration of the silica when no bases other than the alkalis were present. From the last three series of analyses it would seem that some silica always fails to be rendered insoluble by heat alone, so that, if a definite amount of pure silica were taken and subjected to alternate fusions and dehydrations, we should expect that the amount of silica obtained would diminish at each successive treatment. To ascertain if this were so, two determinations of silica were made in the lime slag, and the silica thus obtained repeatedly treated by fusion with alkaline carbonates in the usual way. The per cent. of silica recovered in each case is given below. The silica obtained from the slag by the first fusion and dehydration is taken as 100 per cent.

|    | I.<br>Per cent. | II.<br>Per cent. |  |
|----|-----------------|------------------|--|
| 1. | 42.02           | 41.81            | { Silica in slag obtained by heating to 280°C.                                     |
| 2. | 97.24           | 97.79            |  |
| 3. | 96.04           | 96.70            | { Percentage of the above obtained in four successive fusions by heating to 120°C. |
| 4. | 95.17           | 95.96            |  |
| 5. | 94.19           | 95.45            |  |

The large difference between the results of the first and second fusions is probably due to impurities in the silica, which was heated to 280° C.; but the variations in the other cases can only be due to loss of silica by incomplete dehydration. Still, these are better results than Craig obtained, who does not, however, mention the temperature he used in dehydrating the silica.

The fourth point considered was the possibility of obtaining the silica in a purer state, that is to say, to decrease the amount of the residue left after treatment with hydrofluoric acid. This residue may be due to imperfect washing, or to the fact that alumina has been rendered insoluble in hydrochloric acid by prolonged heating to a high temperature. The higher residues obtained in the cases in which the silica was heated to 280° C. point to the latter possibility. But it is not improbable, as will be mentioned later on, that under certain conditions the silica may enclose alkaline salts so that it is impossible to remove them completely by washing.\*

In an interesting article by Lindo,† on the analysis of glass, I met the recommendation that the watery solution of the fusion be diluted to a very large bulk, so that on acidifying with hydrochloric acid there shall be no precipitation of silica. In this way he obtained, on evaporation, what he called "vitreous silica," in distinction from the ordinary "amorphous silica." This vitreous silica, he says, is so easily washed that time is gained in the analysis to compensate for that lost in the evaporation of the solution. Lindo takes it for granted that one cannot get all the silica by the ordinary process of dehydration, and that the last traces of it cannot be got out of the filtrate unless there

\* In this connection it is interesting to note that all the residues left on treatment with hydrofluoric acid, in the two slags analysed, contained manganese, which may point to an insoluble compound of manganese with the alkaline salts.

† *Chemical News*, Vol. LX., No. 1546.



is sufficient iron oxide or alumina present to effect its complete precipitation. In the analysis of glass, he added a known amount of ferric chloride to the filtrate from the alumina, and by precipitating this iron with ammonia the last traces were obtained.

The following analyses of glass were made according to his directions. The powdered glass, about one gram., was fused with five grams. of sodium and potassium carbonates, and the mass treated with about four hundred cubic centimetres of boiling water until it was thoroughly disintegrated. On acidifying with hydrochloric acid, a

TABLE IV.—DETERMINATIONS OF SILICA IN GLASS. (LINDO'S METHOD.)

|   | I.<br>Silica obtained<br>after<br>two fusions. | II.<br>Residue from<br>Column I. with<br>hydrofluoric acid. | III.<br>Silica obtained from<br>the filtrates. | IV.<br>Total Silica. |
|---|--|---|--|----------------------|
|   | Per cent.                                      | Grams.  | Grams.   | Per cent.            |
| 1 | 73·03  | ·0003   | ·0058  | 73·58                |
| 2 | 71·81  | ·0008   | ·0125  | 73·06                |
| 3 | 72·50  | ·0004   | ·0084  | 73·22                |
| 4 | 71·96  | ·0000   | ·0051  | 71·43                |
| 5 | 71·25  | ·0007   | ·0060  | 71·70                |

clear solution was obtained. This was evaporated to dryness on a water bath, heated to 125° C., and, as recommended by Lindo, the silica thus obtained again fused and treated as before. This silica obtained from the second fusion was weighed, and then treated with hydrofluoric acid. The two filtrates were combined and evaporated to dryness, heated to 125° C. for one hour, and the residue, insoluble in hydrochloric acid and water, filtered off; this is given in the third column. The first three analyses are of German "half-white" glass; the last two of Bohemian white glass.

In this case it is seen that a considerable portion of the silica fails to be dehydrated by one evaporation and heating to 125° C. The silica obtained in this way is very compact, and the washing, as claimed by Lindo, is very easily done. The purity of the silica thus obtained (shown by the small residue left on treatment with hydrofluoric acid) is doubtless in part due to the facility with which the silica is washed; for it is conceivable that, when the silica is separated from a concentrated solution of alkaline salts, it may enclose particles of the liquid which may not be easily washed out. But this high purity, as compared with the silica obtained from the slags and the feldspar, may be due to the absence of any large amount of alumina in the glass.

To see what would be the character of the silica obtained from the first slag by large dilution of the solution of the fused mass before acidifying, the following determinations were made:—

TABLE V.—AMOUNT OF FOREIGN MATTER IN SILICA OBTAINED FROM LIME SLAG.  
(LINDO'S METHOD.)

|    | I.<br>Weight of Silica<br>obtained<br>from Slag.<br>Grams. | II.<br>Residue from<br>Column I. with<br>hydrofluoric acid.<br>Grams. |   |
|----|--|---|---|
| 1. | ·2755  | ·0008   | } Silica obtained by evaporation to<br>dryness on water bath.         |
| 2. | ·2610  | ·0010   |   |
| 3. | ·2871  | ·0008   | } Silica obtained by evaporation to<br>dryness and heating to 125° C. |
| 4. | ·2683  | ·0012   |   |
| 5. | ·2506  | ·0036   | } Silica obtained by evaporation to<br>dryness and heating to 280° C. |
| 6. | ·3113  | ·0043   |   |

These figures would seem to justify the inference that in the presence of considerable alumina it is not possible, even by large dilution, to get as pure silica as is easily obtained when only salts of the alkalies or alkaline earths are present.

The foregoing determinations confirm the statement that the ordinary process of fusion with alkaline carbonates and evaporation to dryness cannot always be relied on to render all the silica insoluble. No experiments were made to determine the effect of repeated evaporations to dryness with hydrochloric acid.

When the evaporation is carried out in the presence of free sulphuric acid the results are more satisfactory, but, as Craig says, the amount of alkaline sulphates introduced seriously interferes with the determination of the bases present.

A comparison of results obtained from a sample of quartz by evaporation with hydrochloric and sulphuric acids is given below:—

| I.   | II.   |
|--|---|
| Silica by evaporation<br>to dryness with hydrochloric<br>acid and heating to 120°. | Silica by evaporation<br>to dryness<br>with sulphuric acid. |
| Per cent.  | Per cent.   |
| 98.95  | 99.43   |
| 98.60  | 99.67   |
| 98.79  | 99.51   |
|  | 99.70   |

In these determinations I followed Lindo's recommendation of diluting largely before acidifying, and the residue left, on treatment with hydrofluoric acid, was very small. The first two determinations by sulphuric acid were done by decomposing the dilute watery solution of the fusion with hydrochloric acid, evaporating to dryness, and then adding strong sulphuric acid in excess and heating on an iron plate until copious fumes of sulphuric acid were given off for several minutes. The silica was in appearance the same as obtained by Lindo's method with the aid of hydrochloric acid only. But in the last two the watery solution of the fusion was decomposed directly by sulphuric acid in considerable excess, and then evaporated as before. The silica obtained in this way was very bulky and gelatinous.

These results seem to justify the recommendation that has been made, namely, that in the analysis of silicates the silica is best determined by dehydration with sulphuric acid (in cases where it is not inadmissible by the presence of lime, barium, lead, etc.), and that the bases should be determined, after the decomposition of the silicate, by hydrofluoric acid.

#### ESTIMATION OF FUSEL-OIL IN SPIRITS.

By A. STUTZER AND O. REITMAIR.\*

IN our former paper on this subject (*Rep. Anal. Chemie.*, 1886), we gave it as our opinion that of the processes from time to time proposed for the determination of fusel-oil in spirits, only two are reliable, viz., the process of Röse (as modified by us), and the capillarity of J. Traube. We then observed that the last process may give too high results if the brandy contains large quantities of ethereal oils. Several colleagues confirmed our experiments and adopted our final process. The minute investigations of E.

\* *Zeitschr. f. angew. Chemie*, Sept., 1890.

Sell also showed our process to be preferable to all others. True, the analysis is easier and more quickly performed with Traube's capillarimeter, but when the spirit is very poor in fusel-oil, the results with Röse's method are more exact. As regards the more recent process recommended by Traube, and called the stalagmometric method, Sell thinks it to give results less reliable than the two just mentioned.

W. Fresenius has recently published a research on the estimation of fusel-oil in spirits of wine, cognac, arrac, and other strong spirits. He used by preference Röse's method with a large shaker, but also employed Traube's two apparatus. Fresenius does not say which of the three processes is the most reliable, but believes the stalagmometer to be the more suitable for such analysts who but rarely have to estimate fusel-oil in spirits. Noteworthy is Fresenius' remark that supposed pure commercial spirits showed a different behaviour, and he says: "Apart from experimental errors, this can only be explained by some spirits containing a substance with properties reverse to those of fusel-oil." If this idea should be confirmed, the whole principle of the two methods would be rudely shaken, because it is always as well to do a check with pure spirit; but what is worse still, it would be possible for a sample to contain a large quantity of fusel and still not show any at all, by the physical processes.

We have once more studied the matter and made it our task to estimate the fusel, not only in brandies (branntweinen), but also in the stronger spirits, with greater accuracy than before. For the testing of spirits, the process adopted for brandies is not sufficiently accurate. It must be remembered that the refining value of spirits is much influenced by minute quantities of fusel, and as the spirit has to be diluted up to 30 or 20 per cent., the experimental errors will be about three times as great as with a sample of brandy with say 30 per cent. of alcohol. E. Sell is certainly of opinion that in the Röse-Herzfeld's apparatus '01 c.c. of increase in the chloroform may be read off with certainty; but, calculated on absolute alcohol, this means '022 per cent. of fusel-oil. As, however, with strong spirits, the error may be two or three times higher, it might easily happen that one analyst declares a sample pure and another finds as much as '1 per cent. of fusel. In our recent investigations we made use of Traube's capillarimeter and also of Röse's shaking apparatus. We thought of getting, in the case of brandies, the best results with Traube's process, because it is not interfered with by ethereal oils. For Röse's process we used the new apparatus of W. Fresenius, which we have seen at work in the laboratory at Wiesbaden. A graduation of the small tube in 0.2 of a c.c. has its drawbacks, as the chloroform collects but slowly in the small tube, which is also difficult to clean. As besides, the larger apparatus is 2.5 times more accurate, an increase of 0.5 c.c. means the same as a ditto of '02 c.c. in the small Windisch's apparatus. A more accurate estimation of the fusel-oil was made possible by first removing part of the pure alcohol, and so getting a product richer in fusel. This succeeded best by a fractional distillation, sometimes with addition of calcined carbonate of potash to retain the water. In cases where the fusel did not exceed '1 per cent. we succeeded in getting a tenfold concentration.

The boiling-point was but little higher than that of absolute alcohol, and remained constant almost to the end of the distillation. The process of distilling will be presently described; the distillates contained a percentage by volume from 95-96.

## GENERAL REMARKS ABOUT THE USE OF THE LARGE SHAKING APPARATUS.

For the calculation of the amount of fusel, we proposed to take the difference between the increase of the chloroform when shaken with a *pure* alcohol and with the sample, and found that the presence of .1 per cent. of amylic alcohol caused an increase of .15 c.c. in the volume of the chloroform. If the temperature exceeded  $15^{\circ}\text{C}.$ , we proposed a decrease, or increase, of .1 c.c. The Government officials, however, were directed not to use the correction for temperature, but to make the experiment at exactly  $15^{\circ}\text{C}.$  We, however, think it best to make a correction at all events if the temperature is very near  $15^{\circ}\text{C}.$

In using the large shaker, the chloroform, of which we use 50 c.c., should be of a temperature of  $15^{\circ}\text{C}.$ ; if possible the 250 c.c. of the alcoholic distillate (of 965.6 sp. gr.) of the same temperature. The refrigerating fluid is most useful when a few tenths under  $15^{\circ}\text{C}.$ , and this must not alter during the experiment. In this manner the temperature of the chloroform is sure not to differ much from  $15^{\circ}\text{C}.$

A. *Correction for Temperature.*—We have made several experiments in this direction. 50 c.c. of chloroform were put into the apparatus, 250 c.c. of the alcoholic fluid were introduced, and finally 25 c.c. sulphuric acid of 1.286 sp. gr.\* After thorough shaking, we waited until the chloroform had completely separated, and then put in the thermometer, which showed  $15.2^{\circ}\text{C}.$  The volume of the chloroform was now 54.7 c.c. The shaking was several times repeated and the volume of the chloroform again noted at various temperatures.

|             |                         |                   |            |
|-------------|-------------------------|-------------------|------------|
| Temperature | $15.5^{\circ}\text{C}.$ | volume chloroform | 54.75 c.c. |
| "           | $15.8^{\circ}$          | "                 | 54.80      |
| "           | $14.1^{\circ}$          | "                 | 54.58      |
| "           | $14.4^{\circ}$          | "                 | 54.61      |
| "           | $14.7^{\circ}$          | "                 | 54.66      |
| "           | $14.9^{\circ}$          | "                 | 54.68      |
| "           | $15.0^{\circ}$          | "                 | 54.69      |
| "           | $15.3^{\circ}$          | "                 | 54.72      |
| "           | $19.3^{\circ}$          | "                 | 55.56      |
| "           | $19.4^{\circ}$          | "                 | 55.56      |

Disregarding experimental errors, the correction for the greatest difference in temperature ( $4.4^{\circ}\text{C}.$ ) is .87 c.c.; consequently .2 c.c. for every degree between the temperatures of  $15^{\circ}$  and  $15.8^{\circ}\text{C}.$ , the allowance is .014 c.c. for every  $.1^{\circ}\text{C}.$ ; between  $14.1^{\circ}$  and  $15^{\circ}\text{C}.$  it is .012 for every  $.1^{\circ}\text{C}.$ ; and for the still lower temperature it only amounts to .01 c.c. for every degree alteration in temperature.

In similar manner, several other experiments were carried out, and finally the correction of .01 c.c. for every degree difference in temperature proposed, provided the temperature does not sensibly vary between  $14.5$  and  $15.5^{\circ}\text{C}.$  The shaking and reading off must be at least twice repeated.

B. *The Check with Pure Alcohol.*—Three samples of alcohol from various sources, the first two bought as pure and absolute, and the third as a pure 96 per cent. spirit, were each experimented upon.

The chloroform was bought as pure, and was not subjected to any purification in our laboratory. The watery solution gave a very faint iodoform reaction. The alcohols

\* Addition of sulphuric acid slightly prevents the solution of pure alcohol in the chloroform.

were at once diluted up to 30 per cent. without previous re-distillation, .1 per cent. strength being considered as within experimental error. The volume of the chloroform in three shakings did not differ more than .03 c.c.

|   |                           | Volume of chloroform 15° C. |                         |
|---|---------------------------|-----------------------------|-------------------------|
| A | purest absolute alcohol   | ...                         | 54.63<br>54.64          |
| B | " " "                     | ...                         | 54.60<br>54.60          |
| C | pure 96 per cent. alcohol | ...                         | 54.62<br>54.65<br>54.64 |

The same alcohols were now re-distilled with pure KHO, and the rectified product again shaken.

|   |     |     |       |
|---|-----|-----|-------|
| A | ... | ... | 54.63 |
| B | ... | ... | 54.60 |

1,000 c.c. of C alcohol were then put into a two-litre retort and slowly distilled from a sandbath, 100 c.c.'s being separately collected. After the distillation was over, about 300 c.c. of water were put into the empty retort, and again distilled until the boiling-point had become constant. The difference between 100° C. and this constant boiling-point was added to the boiling-points of the various fractions, so as to get thorough comparable results unaffected by barometrical pressure variations. The watery distillate was united with the last spiritual fraction. The boiling point of the alcohol kept almost constant (78.6), but only at the very last it got up to 79.5.

The different fractions were now each brought up to 965.6 specific gravity and then shaken out with chloroform, with the following results :

| Fraction.      | Temperature 15° C. |       | Average. |
|----------------|--------------------|-------|----------|
| 1              | 54.82              | c.c.  | 54.74    |
| 2              | 54.69              | "     |          |
| 3              | 54.74              | "     |          |
| 4              | 54.71              | "     |          |
| 5              | 54.57              | "     | 54.51    |
| 6              | 54.53              | "     |          |
| 7              | 54.50              | "     |          |
| 8              | 54.47              | "     |          |
| 9              | 54.50              | "     |          |
| 10             | 54.72              | "     |          |
| Actual average |                    | .. .. | 54.625   |

The fractions from 5 to 9, therefore, gave a decided lower chloroform figure than the first and last fractions, and it seemed, therefore, that our so-called pure alcohol contained impurities. The alcohols A and B were now also submitted to fractional distillation, and the sixth and tenth fractions tested :

|      | Sixth fraction. | Tenth fraction. |
|------|-----------------|-----------------|
| A .. | 54.50           | 54.69           |
| B .. | 54.50           | 54.70           |

From these experiments it is plain that we cannot trust to the purity of commercial alcohol, but that the test-alcohol must be purified by fractional distillation and then tested with the chloroform.

C. *The Increase of the Chloroform Volume by Amylic Alcohol.*—Before attempting to further improve on the method, we first wanted to test its present accuracy. Of alcohol A, a large quantity was diluted up to 30 per cent. by volume, and a mixture was also prepared containing 1 per cent. of amylic alcohol by volume, and which also showed a sp. gr. of 965.6 at 15° C. By mixing the two spirits we got mixtures with definite amounts of amylic alcohol. The shaking was performed as described with chloroform and sulphuric acid.

| Per cent. of Amylic Alcohol. | Volume. | Chloroform. |
|------------------------------|---------|-------------|
| ·0                           | 54.64   | 54.63       |
| ·02                          | 54.72   | 54.71       |
| ·04                          | 54.78   | 54.78       |
| ·06                          | 54.84   | 54.85       |
| ·08                          | 54.91   | 54.92       |
| ·10                          | 54.99   | 55.00       |
| ·20                          | 55.36   | 55.35       |
| ·50                          | 56.48   | 56.47       |
| 1.00                         | 58.32   | 58.31       |

·01 c.c. increase in the chloroform, therefore, corresponds with .0028 per cent. of amylic alcohol. The used apparatus, therefore, is capable of determining .02 per cent. of amylic alcohol, because the difference in chloroform volume for .02 c.c. amylic alcohol — .074 c.c. But on the other hand, an experimental error of .01 per cent. must be allowed for. The liquid actually experimented on occupies about three times the volume of the original alcohol. Therefore, under the most favourable conditions, .06 per cent. may be estimated with fair accuracy in the stronger spirits. And sometimes we may even be in doubt whether such a spirit may not contain .1 per cent., if the check-spirit has not given a very favourable result.

*(To be continued.)*

## THE USE OF ANIMAL CHARCOAL IN THE DETERMINATION OF FAT (ETHER EXTRACT) IN FEEDING STUFFS.

BY H. J. PATTERSON.\*

THE crudeness of the product which goes under the term "ether extract" in fodder analyses is a thing that has impressed itself upon all who have to any extent been engaged in the determination of the various constituents of farm products. How to get rid of a portion, if not all, of this extraneous matter, and have nothing but fat or very closely allied products, has been an interesting question, up to this time unsolved.

To obviate this difficulty I have successfully used animal charcoal, and have obtained a product which in many cases was nearly pure vegetable oil, and in no instance could much foreign matter be detected, getting in every case a product having the general appearance and characteristics of pure fats.

The preparation of the sample and manner of treating the extract has been precisely that adopted by the Association of Official Agricultural Chemists. In filling the percolator tube there was first placed in it the animal charcoal, on top of this a plug of cotton, then the substance to be extracted, and finally another plug of cotton. The

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\* "American Chemical Journal,"

cotton serves to make a more uniform stream of ether over the substance, and keeps the latter from crawling up the sides of the percolator.

The plug between the substance and the charcoal will prevent any of the fat coming in contact with the charcoal before it is thoroughly in solution. In a few instances, especially in the case of grains, it was found that the results were a little too low if the fat came in contact with the charcoal before it was thoroughly held in solution by the ether.

In all cases one gram. of the substance was used. With grains and meals one gram. of charcoal was used, and with hay, fodders, and the like, two grams. The amount of charcoal can be varied at the discretion of the analyst, but the above amounts were found satisfactory. The animal charcoal was a pure article, of medium fineness, thoroughly dried, extracted with ether, and again dried and preserved for use in a well-stoppered bottle. The cotton was of good quality and clean, and had been extracted with ether previous to use.

In the following discussion the method of the Association of Official Agricultural Chemists is designated as Method I., and where charcoal has been employed as Method II.

To prove that there is no loss in passing of pure fat through charcoal, a number of fats were absorbed on cotton and extracted by each of the two methods. The results are given in the following table (A.):—

TABLE A.

| Sample.          | METHOD I.              |                            |                           | METHOD II.             |                            |                           |
|------------------|------------------------|----------------------------|---------------------------|------------------------|----------------------------|---------------------------|
|                  | Fat<br>Added.<br>Gram. | Fat<br>Recovered.<br>Gram. | Loss<br>or Gain.<br>Gram. | Fat<br>Added.<br>Gram. | Fat<br>Recovered.<br>Gram. | Loss<br>or Gain.<br>Gram. |
| Cotton-seed oil, | ·2180                  | ·2180                      | 0000                      | ·1770                  | ·1760                      | —·0010                    |
| "    "           | ·2020                  | ·2025                      | +·0005                    | ·2015                  | ·2010                      | —·0005                    |
| "    "           | ·2015                  | ·2010                      | —·0005                    | ·1815                  | ·1810                      | —·0005                    |
| Average,         | ·2072                  | ·2072                      | 0000                      | ·1867                  | ·1860                      | —·0007                    |
| Butter,          | ·1775                  | ·1770                      | —·0005                    | ·1765                  | ·1760                      | —·0005                    |
| "    "           | ·1520                  | ·1510                      | —·0010                    | ·1880                  | ·1870                      | —·0010                    |
| "    "           | ·0910                  | ·0910                      | 0000                      | ·1030                  | ·1035                      | +·0005                    |
| Average,         | ·1402                  | ·1397                      | —·0005                    | ·1558                  | ·1555                      | —·0003                    |
| Mutton tallow,   | ·1160                  | ·1165                      | +·0005                    | ·1470                  | ·1480                      | +·0010                    |
| "    "           | ·0960                  | ·0960                      | 0000                      | ·0925                  | ·0930                      | +·0005                    |
| "    "           | ·0970                  | ·0970                      | 0000                      | ·0810                  | ·0815                      | +·0005                    |
| Average,         | ·1030                  | ·1032                      | +·0002                    | ·1068                  | ·1075                      | +·0007                    |
| Lard,            | ·0675                  | ·0670                      | —·0005                    | ·1415                  | ·1420                      | +·0005                    |
| "    "           | ·1345                  | ·1340                      | —·0005                    | ·0925                  | ·0930                      | +·0005                    |
| "    "           | ·2330                  | ·2325                      | —·0005                    | ·0660                  | ·0660                      | 0000                      |
| Average,         | ·1450                  | ·1445                      | —·0005                    | ·1000                  | ·1003                      | +·0003                    |
| Beef tallow,     | ·1100                  | ·1100                      | 0000                      | ·1125                  | ·1120                      | —·0005                    |
| "    "           | ·1515                  | ·1520                      | +·0005                    | ·1545                  | ·1540                      | —·0005                    |
| "    "           | ·0965                  | ·0965                      | 0000                      | ·1335                  | ·1335                      | 0000                      |
| Average,         | ·1193                  | ·1195                      | +·0002                    | ·1335                  | ·1332                      | —·0003                    |
| Sum of averages, | ·7147                  | ·7141                      | —·0006                    | ·6828                  | ·6825                      | —·0003                    |

From this table it will be seen that there is no appreciable loss, and that the two methods are about the same when pure fats are being extracted. The different fats

employed give about as much range in composition and physical characters as would be expected in the various vegetable fats.

In Table B. is given a comparison of the two methods on a variety of samples, which cover fairly well the different classes of substances met with in agricultural analysis. A comparison of the results given in table B. shows that there is a difference in every case, Method I. giving the higher result, and in some cases the difference is surprising. This shows that the amount of error which has been introduced into our valuations of feeding stuffs, calculation of digestibility and nutritive ratios, is very much more exaggerated and misleading than has been supposed. The results in Table B. are the average of triplicate determinations.

TABLE B.

| Description of Sample.                                     | I.                | II.               | Difference.<br>Per Cent. |
|--|-------------------|-------------------|--------------------------|
|  | Per Cent.<br>Fat. | Per Cent.<br>Fat. |                          |
| Clover hay .. .. .   | 3.51              | 2.02              | 1.49                     |
| Corn fodder .. .. .  | 6.17              | 2.69              | 3.48                     |
| Corn meal .. .. .  | 4.63              | 4.53              | 0.10                     |
| Cotton-seed meal .. .. .                                   | 10.50             | 9.88              | 0.62                     |
| Dung from digestion experiment on cotton-seed meal .. .. . | 5.83              | 3.83              | 2.00                     |
| Oats hay .. .. .   | 4.12              | 2.57              | 1.55                     |
| Soja bean silage .. .. .                                   | 5.53              | 4.70              | 0.83                     |
| Sorghum fodder, "Early Orange" .. .. .                     | 5.46              | 2.70              | 2.76                     |
| Sorghum silage, "Amber" .. .. .                            | 6.15              | 3.68              | 2.47                     |
| Tomatoes (dried) .. .. .                                   | 10.07             | 6.48              | 3.59                     |
| Unknown pea .. .. .  | 3.44              | 1.76              | 1.68                     |
| Wheat bran .. .. .   | 3.80              | 3.33              | 0.47                     |

Having noticed the acidity of the smell of the extract of some of the samples and of ether which was distilled from the extract of some plants, a few tests of the amount of acid in the extracts, soluble in cold water, were made by titrating it with decinormal sodium hydrate, phenolphthalein being used as an indicator. In nearly every case some acid was found in the extract of Method I., reaching over 1 c.c. in some cases, there being scarcely a trace from the extract of Method II. The only case in which there was an appreciable amount of acid in the extract of Method II. was from the sorghum silage.

From a study of these figures and a close examination of the products obtained by the two methods, it seems that the use of charcoal results in a closer approximation to the truth than any other method in use, though absolute accuracy is not claimed. The following points may be rightly claimed in favour of the use of animal charcoal in the determination of fat (ether extract) in feeding stuffs.

- (1) That the product obtained is nearly pure fat or vegetable oil.
- (2) That the product obtained gives a more correct idea of the physical nature of the fats from various substances.
- (3) That slight quantities of water that may exist in the substance and pass out with the extract will be removed by the charcoal.
- (4) That soluble acids of the plant, or acid which may be formed by the continuous distillation of ether, in connection with some constituents of plants, will be partially, if not wholly, removed by the animal charcoal.
- (5) That the animal charcoal will partially obviate, if not wholly remove, the difficulty of change in the amount of ether extract (which generally increases) with the aging of the sample.

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REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN  
ANALYTICAL PROCESSES.

ANALYSES OF EAST INDIAN HONEYS. VAN DER MARCK. *Ned. Tydschr. v. Pharmacie*, etc., September, 1890.

| Name.           | Spec. gravity at<br>12° C. | Colour.         | c.c. of a 10 per cent. solution<br>by volume required to reduce 10 c.c.<br>Fehling. |                  | Polarisation of 10<br>per cent. solution in<br>20 c.m. tube. | Ash per cent. |
|-----------------|----------------------------|-----------------|---|------------------|--|---------------|
|                 |                            |                 | Before inversion.   | After inversion. |  |               |
| —               | 1.3134                     | Yellow          | 9   | 8.5              | + 13'  | .26           |
| Mengkepar ..    | 1.3546                     | Brown           | 7.2   | 7.2              | - 2°54'  | .39           |
| Plarvan ..      | 1.3426                     | Dark Brown      | 7.6   | 7.6              | - 52'  | .54           |
| Pelas ..        | 1.3099                     | Yellow          | 8.0   | 8.0              | - 3'   | .12           |
| Tjeret Madce .. | 1.3569                     | Light Brown     | 6.9   | 6.9              | - 1°53'  | .43           |
| Tarvon Blora .. | 1.3586                     | Very Dark Brown | 6.7   | 6.7              | - 1°36'  | .39           |

Applying the usual equation, the author finds the composition

| of No. 1 | Glucose. |  | Levulose. |
|----------|----------|--|-----------|
|          | 28.70    | 22.90 (in addition 3 per cent. of saccharose.) |           |
| " 2      | 24.60    | 39.60  |           |
| " 3      | 31.11    | 29.99  |           |
| " 4      | 32.90    | 25.20  |           |
| " 5      | 30.80    | 36.60  |           |
| " 6      | 33.30    | 36.62  |           |

The acidities of the samples were respectively 1.8, 1, .2, .2, .2, .4 c.c.  $\frac{N}{10}$  soda. Their ashes required .6, 2.4, 3.6, .1, 3.0, 2.6 c.c.  $\frac{N}{10}$  oxalic acid.

I. DE K.

ESTIMATION OF ZINC IN SILICEOUS ORES CONTAINING LEAD. DR. W. MINOR. (*Chem. Zeit.*, No. 61).—Two grams. of the ore are boiled for fifteen minutes with 60 c.c. of weak soda ley. After pouring off, the insoluble matter is again boiled with soda. The liquid is filtered off and the residue washed with boiling weak soda. The filtrate is acidified with sulphuric acid, which causes any lead to separate as sulphate. Water is now added up to a definite bulk, and after standing for a few hours, half of the volume is filtered off, and after mixing with excess of ammonia titrated with standard sodium sulphide. No notice need be taken of the little alumina which generally forms on adding the ammonia. By this process we only get the zinc in combination with carbonic or silicic acid, but not the sulphide. L. DE K.

ASSAY OF RAW MATERIALS CONTAINING TARTARIC ACID. DR. LAMPERT. (*Chem. Zeit.*, No. 55).—This analysis is not always reliable. The author mentions an instance where the same sample was analysed five times by a leading analyst and gave results varying from 23 to 33 per cent., whilst differences of 2 or 3 per cent. are quite common when the assay is performed by Goldenberg's process. This process in itself is exceedingly accurate, so the bad results sometimes obtained have been ascribed to the presence of organic matter. But although pectin for instance may influence the result a little, it is not to be held responsible for the serious differences just mentioned. The author after a long investigation at last found the enemy to be alumina, which if present in large quantity entirely upsets Goldenberg's process. Experiments on known mixtures showed a deficiency of 5 per cent. of tartaric acid when the mixture contained 25 per cent. of alum, 9.5 per cent. when 45 per cent. of alum was present, and 15.5 per cent. if the alum reached 50 per cent. The author also found the reason why the same chemist got such varying results with the same sample. It is because the loss in tartaric acid not only depends on the amount of alumina but also on the amount of acetic acid used. The author has invented a process which almost entirely removes the alumina from tartaric liquors. Liquids so treated showed 80 per cent. of tartaric acid instead of 49, and no serious differences were noticed on submitting the same sample to different analysts. Unfortunately the author does not give any details of his important process. LE DE K.

ARSENIC TEST.—The behaviour of the hypophosphites towards arsenical solutions (precipitation of metallic arsenic) is brought into prominence again by G. Looff as a test for arsenic; in sensitiveness it ranks between the tests of Gutzeit and Bettendorf. Ten c.c. hydrochloric acid, of any strength or purity, with 0.2 gram. calcium hypophosphite placed in a water-bath for 1-2 hours, will enable the detection of  $\frac{1}{10}$  milligram. arsenic (Bettendorf's test will detect  $\frac{1}{30}$  milligram.). Five c.c. sulphuric acid, phosphoric acid or glycerin, with 0.2 gram. of a hypophosphite (in the presence of sulphuric acid the sodium salt is best used, in other cases the calcium salt, because of its non-hygroscopic character) and 10 c.c. concentrated hydrochloric acid warmed in a water-bath for 1-2 hours will show the presence of  $\frac{1}{10}$  milligram. arsenic. Of calcium phosphate, sodium phosphate and tartar emetic, 0.5 gram. is dissolved in 10 c.c. concentrated HCl and 0.2 grams. calcium hypophosphite added, etc. Bismuth subnitrate must first be ignited to remove the nitric acid, and then proceeded with as above; or dissolve equal weights

of the subnitrate and hypophosphite in hydrochloric acid and warm. Sulphide of antimony is dissolved in HCl with the aid of a little potassium chlorate before adding the hypophosphite and warming. To test solution of ferric chloride, a combination of Bettendorf's test and the hypophosphite test allows the detection of the smallest trace of arsenic: 5 c.c. of the solution mixed with 10 c.c. HCl are decolorised by addition of Bettendorf's test solution, then the hypophosphite added and warmed. Most of the commercial solutions of ferric chloride were found to contain arsenic.—*Am. Journ. Pharm.*

A MORPHIOMETRIC ASSAY OF OPIUM, for which is claimed purity of the morphine obtained, the alkaloid being almost white and immediately soluble in 100 parts lime water, considerable saving of time, and, constant results, the extreme differences of a number of essays being within 0.3 per cent. (the results of this method are always about 1 per cent. lower than by Dieterich's method) is as follows: 5 grams. of the finely powdered opium are triturated with water and made up to 78 grams.; after frequently agitating during 1-2 hours, 60.8 gram. (representing 4 grams. opium) are filtered off, and in it dissolved 0.2 gram. oxalic acid. After one half-hour, 5.2 grams. of a solution of potassium carbonate (1 : 2) are added, thoroughly mixed (avoiding unnecessary agitation) and 16.5 grams. filtered at once through a dry plaited filter of 12 cm. diameter into a tared flask of 30 c.c. capacity. To the 16.5 gram. filtrate (representing 1 gram. opium) add 5 grams. ether free from alcohol, cork the flask and agitate briskly for ten minutes; the ether is then evaporated by use of a small rubber blast, the morphine collected on a small plain filter and thoroughly washed with water saturated with ether, dried at 40-50° C., returned to the flask, which has been dried in the meantime, and weighed to constant weight.

The addition of the oxalic acid is made to precipitate calcium salts, which are present in all opium varieties excepting Salonica opium, which gives no perceptible precipitate; by the use of a large excess of potassium carbonate the narcotine is completely and immediately precipitated, while no morphine is precipitated in the minute's time necessary to filter off the 16.5 gram. filtrate.

This method has also been applied to the examination of *extract* and *tincture of opium*. 2.5 grams. *extract* are dissolved in water, with the addition of 0.2 gram. oxalic acid, diluted to 70 grams., 5 grams. solution of potassium carbonate added, 15 grams. filtered off (corresponding to 0.5 gram. *extract*., etc., as above).

Fifty grams., with 0.2 gram. oxalic acid, are evaporated to a thin *extract* and gradually diluted with water to make 70 grams.; to this add 5 grams. solution of potassium carbonate, and filter off 15 grams. (corresponding to 10 grams. *tincture*), and proceed as above.—*Am. Journ. Pharm.*

THE DETECTION OF NITROBENZOL OR OIL OF MIRBANE in oil of bitter almonds succeeds easily by warming the suspected oil with black oxide of manganese and sulphuric acid. Nitrobenzol does not lose its odour by this treatment, on the contrary, the odour becomes more pronounced, after standing for awhile an odour of oil of cinnamon is developed; oil of bitter almonds at first develops a disagreeable odour, which, after some time, entirely disappears.

To detect nitrobenzol in soaps, solutions, etc., soaps are first dissolved in water; the solutions are treated with an excess of slaked lime, extracted with ether, the ethereal solution evaporated to dryness on a water-bath, and the residue shaken up with a little water. In a small porcelain capsule are placed two drops liquefied carbolic acid (made by adding 10 parts water to 100 parts of the crystallised acid), three drops distilled water, and a piece of potassium hydrate of the size of a pea. This mixture is heated to the boiling point, care being taken to prevent charring of the mass, and a few drops of the ethereal residue mixture added; on continued boiling, a carmine-red ring is formed around the edge of the liquid, the depth of colour depending upon the quantity of nitrobenzol present; the addition of calcium hypochlorite solution changes the red into a beautiful green colour.—J. MORPURGO, *Pharm. Post.*

## CORRESPONDENCE.

[The Editor is not in any way responsible for opinions expressed by his correspondents.]

To the Editor of the ANALYST.

SIR, During the last few months considerable attention has been attracted among public analysts to the largely-increasing substitution by grocers of an imitation article for the well-known Demerara yellow crystals, and as considerable misconception appears to exist in analytical circles as to these, it has occurred to me that a few words on the subject from one who has been closely associated with the manufacture of the real product for some years may not come amiss to your readers.

The term "Demerara crystals" is applied to the yellow crystallised grocery sugar coming from the colony of British Guiana (of which Demerara forms a part). Recently a similar sugar has also been produced by some of the West India Islands, where the Demerara process of manufacture has been adopted.

The peculiarity of this sugar is that, although it may be said to be refined—containing, as it does, from 95 per cent. upwards of sucrose, according to the degree of dryness required by market considerations, the characteristic smell and sweetness of the cane juice has been to a large extent preserved. To secure this end, a process has to be adopted of a special nature, and a product is thus obtained which on account of its possessing the attributes mentioned above, commands a relatively high price in the sugar market, where only sugar coming under the above definition is sold as such.

In order that the essential features of this specific sugar may be readily grasped, it may be as well to briefly describe the principal points in the manufacture, especially those in which the divergence from the general lines of sugar-making occurs.

As doubtless your readers are aware, cane juice consists chiefly of a solution of sucrose, with small and varying proportions of glucose, albuminous pectinoid and mineral matters, etc., and with a colouring matter, *yellow* when free and *green* when united with bases, with which it forms feeble combinations.

As the cane juice comes from the mill, it is treated with sulphurous anhydride, prepared by burning sulphur in a current of air. Distinct acidity is thus imparted to the juice, and the colour of this, which, as it came from the mill, was dirty yellow, is now changed to a delicate greenish-yellow. This change of colour is due to the decomposition of the green colouring compound mentioned above, by the organic acids set free by the sulphurous acid.

The juice is now raised to a temperature of from 212° F. to 225° F. in a closed vessel through which a constant stream of juice is passing, and on emerging is treated with milk of lime, to effect precipitation of the albuminous matter. The smallest quantity of lime that will give a juice sufficiently clarified for subsequent crystallisation is used, so that the colouring matter may be preserved as much as possible in its free—and yellow—state; but unavoidably, to a greater or less extent, according to the purity of the juice, the colour of the clear product drawn off from the subsided precipitate is of too green a colour to yield a high-class yellow sugar. Indeed, should, at this stage of the manufacture, sufficient lime be added to make the juice distinctly alkaline, although a bright clarification would be obtained, the colouring matter would be too much acted upon for any subsequent process to rectify.

In the old method of manufacture, where the concentration of the thin juice from the clarifiers to the state of syrup ready for the vacuum pan was carried out under atmospheric pressure on the costly and destructive "copper wall"; the acidity produced by the passing over this, with its high temperature and tumultuous treatment, rectified to some extent this lime effect on the colouring matter, especially if the concentration were carried far during this process; but this end was only attained by great loss in manufacture from immersion, etc.

In the present method, evaporation in vacuo takes the place of the "copper wall," and as, during this stage, if properly conducted, no chemical change of any moment takes place, the colouring effect of the lime has to be nullified before the juice is subjected to concentration. This is done by the

addition of phosphoric acid to the clear liquor from the clarifiers, and subsequent brief ebullition in what are known as "eliminators." This agent is added in sufficient quantity to liberate enough of the organic acids to recall the yellow colour which the juice possessed prior to the addition of the lime, and, at the same time, a considerable quantity of the lime, whose organic salts are prejudicial in sugar-making, is got rid of. Care, however, must be taken, and this applies equally to the "sulphuring" in the first stage of manufacture, that enough is not added to give rise to free phosphoric acid in the liquor, which would lead to loss later on.

Concentration of the liquor, which has received the finishing cleansing touches during its stay in the "eliminators," is now carried on in vacuo in some form of "multiple effect" until a density of from 25° to 35° Baumé is arrived at. A light, yellow-coloured syrup is thus obtained, which is immediately further concentrated and granulated in the vacuum pan.

When this operation is finished, a stiff magma of crystals and "mother liquor" or molasses, of a delicate greenish gold colour is obtained, and to further improve upon and fix, as it were, this colour, a solution of stannous chloride, in the proportion of about 1·3 lbs. of the latter to a ton of sugar is added. This magma or "massenite" is now subjected to a separating process in the centrifugals, and the light yellow crystals thus obtained, the greater portion of the tin passing away in the molasses.

It is thus seen, and I wish to particularly impress this upon your readers, that the colouring matter of Demerara crystals is emphatically the colouring matter of the cane juice, and that the great object of the manufacture is to retain this colouring matter, and at the same time to produce a sugar of high saccharine richness.

And it is in doing this that another distinctive feature of this class of sugar is yielded, viz., the characteristic smell of cane juice which it possesses. It is owing to these qualities—colour, smell, and richness—that Demerara sugar holds the position it does in the sugar-making world.

A high-class yellow Demerara sugar, therefore, necessitates the use of a minimum quantity of lime, and the maintenance of a high degree of acidity throughout the process. I leave it to those practically acquainted with the working of cane juice to realise the difficulties associated with satisfactory manipulation on these lines, especially with the immature juice frequently met with in Demerara. Suffice it to say that, by efficient machinery and by careful and thoughtful work, it is possible to obtain results as regards the quantity of sugar extracted from the juice as good as those derived from the easier paths of the manufacture of refining crystals.

As already stated, these crystals occupy a high position among sugars in the home markets, and the result of this has been the production, by several refiners here, of distinct and avowed imitations, which, although sold in the market as "refiners' yellow crystals," are eagerly bought up by the trade and handed over to the consumer as "Demerara yellow crystals."

To produce these imitations, all that the refiner has to do is to purchase refining beet sugar, recrystallise it, if necessary, so as to produce the crystalline condition of the Demerara sugar, and colour it, as it is admitted that it is coloured, by a preparation of a yellow aniline product, which possesses an aromatic odour, and which thus masks, when fresh, the characteristic unpleasant smell of beet sugars.

There is thus obtained, instead of a cane sugar possessing the actual colouring matter and smell of cane juice, a product prepared of inferior material and artificially coloured so as to simulate the real article.

This fraudulent substitution of an imitation for a real article goes on to an enormous and increasing extent. *Ceteris paribus*, it is bought for less in the market and retailed as the higher priced and genuine product.

The present position thus is, that the West Indian proprietors, after investing enormous capital in the form of machinery and skilled labour, in order to produce a pure and attractive sugar, find themselves compelled to undergo competition in the very market in which it would be thought their rights would be recognised, with adversaries who are allowed to carry on a trade in an imitation and inferior article with impunity.

There is one point in connection with the manufacture of Demerara sugar which may need comment, and that is, the use of a tin salt in the penultimate stage of the process. The use of this agent was commenced in 1881, but it was not until the following year generally adopted, on account of the uncertainty, from want of evidence, of the physiological position of small quantities of tin, the West India Committee having, in the meantime, investigated the question carefully, and satisfied themselves, by the evidence of Dr. Stevenson, Messrs. Hehner, Wigner, and others, that no fear need be entertained that a prejudicial influence on health would arise from the small quantities—from 25 grains to 33 grains to the lb.—of this metal found to be present in the sugars thus made. Dr. Stevenson, in experiments on dogs, carried out at the instance of the Committee, found that, with a diet almost entirely composed of the sugar in question, no interference whatever with health had resulted. Since then, some 500,000 tons have been consumed in the United Kingdom, without a single ill effect having been traced to its use.

Apologising for trespassing so far on your valuable space,

I am, Sir, faithfully yours,

FREDERIC J. SCARD,

Chemist-in-chief to the Colonial Company, Limited.

16, Leadenhall Street, E.C.,

# THE ANALYST.

NOVEMBER, 1890.

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### A RAPID METHOD FOR THE ESTIMATION OF UREA IN URINE.

By C. J. H. WARDEN, PROF. CHEMISTRY, MEDICAL COLLEGE, CALCUTTA.

As Sutton has remarked, the sodic hypobromite method of estimating urea in urine has given rise to endless forms of apparatus, the principle of construction being in all similar. In all the instruments hitherto proposed, with the exception, I believe, of Lunge's nitrometer, when it is used for the estimation of urea, the decomposition of the urea by the hypobromite has been accomplished in one apparatus, and the evolved gas measured in a separate tube. In the method now described the evolved nitrogen is measured in the same tube used for the decomposition of the urea; and the procedure is consequently much simplified.

The apparatus used for the decomposition of the urea and measurement of the liberated nitrogen, consists of a slightly modified form of Crum's well-known nitrometer. Crum's tube, as usually constructed, has a total length of 210 mm., an internal diameter of 15 mm., and a capacity of about 25 c.c., the cup at the top having a capacity of a little over 2·5 c.c. The modifications desirable in adapting the tube for the estimation of urea may be thus summarised:

(A) Trebling the length of the tube, and thus making it 630 mm. long. The capacity being increased to 75 c.c.; while the internal diameter is not altered.

(B) Grinding on to the lower open end of the tube a glass stopper on which ten narrow grooves have been filed.

(C) Increasing the capacity of the small cup at the top of the tube to 5 c.c., and leaving it accurately graduated to hold 2·5 c.c. when filled to a certain mark.

(D) Using somewhat thinner glass than that employed in the construction of Crum's tubes, as no mercury is employed in the process.

It was found by Russell and West that 5 c.c. of a 2 per cent. solution of pure urea evolved 37·1 c.c. of nitrogen, and this volume was taken as the basis of graduation of the measuring tube. In the process now being described only 2·5 c.c. of urine are used, and as 2·5 c.c. of a 2 per cent. urea solution evolve 18·55 c.c. of nitrogen, this volume of gas will necessarily be equivalent to 2 per cent. of urea. One per cent. of urea is

therefore equal to 9.27 c.c. of nitrogen, and the 9.27 c.c. volume is divided into ten equal parts, each part being equal to 1 per cent. of urea. These divisions are further subdivided into two, each representing .05 per cent of urea. The graduations should be continued so as to indicate up to 3 per cent. of urea. All calculations are thus avoided, the observed volume of gas at once indicating the percentage of urea in the specimen of urine under examination.

In using the apparatus the following solutions are required :

1. A cold aqueous saturated solution of common salt.
2. Hypobromite solution made by dissolving 100 grains caustic soda in 750 c.c. of distilled water and adding 25 c.c. of bromine. This solution should be freshly prepared in small quantities as required for use.

To use the apparatus, the stop-cock should be first slightly greased and closed, the tube inverted, and the ground stopper removed. The hypobromite solution is then poured into the tube to overflowing, the stop-cock opened to allow a drop or two to escape and thus displace the small column of air in the bore of the stop-cock. The grooved stopper is then pressed home, the excess of hypobromite solution escaping by the grooves in the side of the stopper, in the same manner as the superfluous fluid escapes through the capillary orifice in the stopper of a specific gravity bottle. In this way the tube is filled with the hypobromite solution, all air being excluded. The tube is now inverted, held under a tap of water, and the cup, etc., thoroughly washed and then most carefully dried.

The tube is now stood in a small trough of urine—a finger-bowl answers very well—and supported by a filter-ring or clip. The sample of urine to be examined is then poured into the dry cup up to 2.5 c.c. graduation, any excess of urine accidentally introduced being removed by a fine fold of blotting paper. The cup is then filled up with brine, which is well mixed with the urine by a small and slender glass rod. The object of diluting the urine with brine is to increase its density. If ordinary urine were introduced into the tube it would float upon the surface of the hypobromite and only a slight reaction would immediately occur at the point of junction of the two fluids, but by increasing the specific gravity of the urine in the way indicated, it flows through the hypobromite solution, and brisk effervescence ensues. If the urine solution were allowed to enter the tube while closed with the grooved stopper, a portion of the evolved gas would escape through the bore in the stop-cock. In order, therefore, to avoid loss of gas from this cause, the grooved stopper is first removed before urine is allowed to escape from the cup into the tube. In allowing the urine to enter the tube, the stop-cock should be opened sharply and a small amount of urine in a full stream allowed to enter; decomposition of the urea at once ensues, and the gas collects at the top of the tube. When effervescence has ceased, more urine is introduced, and so on, until the cup has been emptied. The cup is then filled with 2.5 of dilute brine, and rinsed round by means of the glass rod; the whole of this brine is then allowed to enter the tube at one operation. The same amount of diluted brine is then again placed in the cup, rinsed round, and allowed to enter the tube. The tube is now grasped by the right hand, the thumb being tightly pressed against the open end, and the contents thoroughly agitated.

Lastly the tube is placed in a vessel of water, and the thumb removed, when the saline solution flows out, and water occupies its place. If, while the open end of the tube is below the surface of water, water from a tap be allowed to flow down the tube, the temperature of the gas will be rapidly reduced to that of the water. The remaining operation consists in measuring the volume of gas with the usual precautions, such volume indicating the percentage of urea without the trouble of any calculation. Corrections for temperature and pressure can, of course, be applied if necessary.

In using the tube, if the evolved gas should exceed the volume yielded by 3 per cent. of urea, the urine must first be diluted with an equal volume of water, and 2.5 c.c. of the diluted urine, and in the manner already described; the percentage of urea as indicated by the volume of gas being doubled.

The points to which special attention may be drawn in connection with this method of estimating urea, are—

1. Extreme simplicity of apparatus; all the various operations, of measuring the urine, decomposing the urea, and measuring the volume of evolved gas, being performed with one instrument.

2. Ease and rapidity of manipulation.

3. Results as accurate as those afforded by any of the various modifications of Russell and West's original method.

Messrs. Cetti and Sons, of Brooke Street, Holborn, are prepared to supply these modified Crum tubes, with a guarantee that the graduations are accurate.

## ESTIMATION OF FUSEL-OIL IN SPIRITS.

BY A. STUTZER AND O. REITMAIR.

*(Continued from page 193.)*

### THE CONCENTRATION OF THE FUSEL BY FRACTIONAL DISTILLATION.

THE possibility of removing the fusel from strong spirits by fractional distillation has often been talked about. Whether portions absolutely free from fusel could thus be obtained was not really proved, because there was no known reliable method to positively detect the presence of amylic alcohol in spirits of wine. An old test consisted in the oxidation of the fusel to valeric acid and analysing one of its salts. The process of Marquard, consisting in shaking first with chloroform, and then washing this with water, does not give good quantitative results. However, our chloroform process enables us to detect very small differences in fusel, and has been very useful in determining the value of the fractional distillation.

It is quite certain that when applying the process to very strong alcohols, products are at last obtained which cannot be further purified. We must, therefore, consider these fractions free from fusel as long as we do not succeed in proving its presence by other means, and ought only to use such a product as a check spirit in our process. For the carrying out of the following experiments, however, it was, as will be easily understood, not necessary to use such a highly purified spirit, but use was made of our spirit C.

Mixtures were made which contained respectively, .1, .05, and .02 per cent. of amylic alcohol. In each case 1,000 c.c. of the sample were distilled, and 100 c.c. separately collected. The boiling points of the first nine fractions were constant between 78.5° and 78.9° C.



## AMOUNT OF AMYLIC ALCOHOL BY VOLUME IN ORIGINAL ALCOHOLS.

| Fraction. | A<br>·10     | B<br>·15     | C<br>·02     | D<br>None    |
|-----------|--------------|--------------|--------------|--------------|
|           | V. 15 = c.c. | V. 15 = c.c. | V. 15 = c.c. | V. 15 = c.c. |
| 1         | 54·80        | —            | —            | 54·82        |
| 5         | 54·56        | —            | —            | —            |
| 7         | 54·51        | —            | —            | —            |
| 8         | 54·53        | —            | —            | —            |
| 9         | 54·50        | 54·52        | 54·51        | 54·50        |
| 10        | 55·74        | 55·09        | 54·82        | 54·72        |

The difference between V. 15 of the ninth and tenth fraction amounts to

|      |     |     |     |
|------|-----|-----|-----|
| 1·24 | ·57 | ·31 | ·22 |
|------|-----|-----|-----|

According to the former analysis, an increase of ·01 c.c. must be considered equivalent to ·0028 c.c. of amylic alcohol. Therefore A contains ·347, B ·161, C ·087, and D ·062 per cent. As, however, the distillates had first to be diluted up to 320 c.c. before applying the process, the true percentage of amylic alcohol becomes

A 1·1104, B ·5152, C ·2784, D ·1984.

If we now deduct the amount found in D we get

A ·912, B ·3168, C ·08 c.c.

The bulk of the fusel is therefore found in the last fraction, and if the spirit is very poor in alcohol it is advisable not only to distil one, but even two or three litres of the sample and operating on the last 100 c.c.

To answer the question in how far the distillation process succeeds when the spirit is not very strong, and in how far dehydraters influence the result, the experiment (A) was repeated, only with this difference, that the mixture was first mixed with 200 c.c. of water, and the alcoholic strength thereby reduced to 80 per cent. (experiment E). In another experiment (F) this same spirit was first mixed with 50 grams. of calcined potash, and in a third experiment (G) with 150 grams. of this substance. The several fractions showed the following boiling points:—

|    | E<br>80 Per Cent. Spirit<br>without Potash. | F<br>Same with<br>50 grms. Potash. | G<br>Same with<br>150 grms. Potash. |
|----|---|------------------------------------|-------------------------------------|
| 1  | 79·3°                                       | 78·8°                              | 78·6°                               |
| 2  | 79·4°                                       | 79·0°                              | 78·6°                               |
| 3  | 79·6°                                       | 79·0°                              | 78·6°                               |
| 4  | 79·8°                                       | 79·1°                              | 78·6°                               |
| 5  | 79·9°                                       | 79·2°                              | 78·6°                               |
| 6  | 80·0°                                       | 79·3°                              | 78·6°                               |
| 7  | 80·1°                                       | 79·4°                              | 78·6°                               |
| 8  | 80·2°                                       | 79·5°                              | 78·6°                               |
| 9  | 80·7°                                       | 79·7°                              | 78·6°                               |
| 10 | 81·2°                                       | 79·9°                              | 78·7°                               |

The separate fractions of G contained from 95 to 96 per cent. of pure alcohol, and the last fraction measured about 100 c.c. The distillates of F had a smaller percentage of alcohol, and those of E were still weaker. Therefore from E and F another 11th fraction was collected, boiling from 81·3° to 80·2° C.

The chloroform shaking gave the following results:—

| Fraction. | E<br>c.c. | F<br>c.c. | G<br>c.c. |
|-----------|-----------|-----------|-----------|
| 9         | 54·63     | 54·55     | 54·51     |
| 10        | 54·64     | 54·69     | 55·76     |
| 11        | 55·13     | 55·71     | —         |

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The volumes of the last fractions of the spirits after proper dilution were—

E 320 c.c.      F 260 c.c.      G 310 c.c.

If we now deduct the increase of the chloroform of A we get

E .41 c.c.      F .99 c.c.      G 1.02 c.c.

which corresponds with .1148, .2772 and .2856 per cent. of amylic alcohol in a 30 per cent. spirit.

The quantity of amylic alcohol in the last fraction is therefore—

-E .368      F .721      G .885 c.c.

and the loss in fusel—

.632      .279      .115

or calculated on 80 per cent. spirit—

.053      .023      .01

It is therefore plain that on using a dehydrater, even a weaker spirit may be made to retain the bulk of its fusel till the last fraction. It is, however, necessary to use a large excess of potash, which quantity must, of course, be regulated by the amount of alcohol the sample contains. As the greater part of the fusel remains in the retort, it is necessary to finally dissolve the potash in water, and then to distil another 100 c.c. The liquid having a high boiling point, all amylic alcohol passes out in the distillate which is then used to dilute the last alcoholic fraction. In the beginning of the distillation we use a brine bath, but at the last the naked flame, or else a paraffin bath. The loss in amylic alcohol, which must be expected from the use of potash, is only .01 per cent. of the whole amount present. W. Fresenius says the smell, either before or after fractioning of the various distillates, is qualitatively a better proof for the presence or absence of fusel than the chemical or physical processes, but this view is not confirmed by our experiments. We found, in fact, that whenever fusel can be detected by the smell, it is quite possible to quantitatively determine it, but if the amount is supposed to be very small, we use, as already stated, not one litre, but even two or three litres of the sample for the fractional distillation.

### OUR EXPERIENCES ON THE FRACTIONAL DISTILLATION OF SPIRITS CONTAINING MUCH FUSEL.

If the sample contains so much fusel that it may be safely detected without a fractional distillation, the experimental error, increased by the necessary dilution, amounts to about .06 per cent. Analysts will have to be content with this degree of accuracy when analysing very bad spirits. The separation of the sample in fractions free from fusel, and those richer in it, then becomes more and more impossible. When distilling one litre of alcohol with .05 per cent. of fusel, only the last 50 c.c. are contaminated; with .1 per cent. the last 100 c.c., with .15 per cent. the last 300 c.c., and with .2 per cent. the last 500 c.c. And if the amount of fusel reaches .5 per cent. the first 300 c.c. of the distillate are already contaminated.

It will now be understood why it is so difficult to purify spirits on the larger scale, as this can only be done by the most improved distilling apparatus and aid of chemical means. The process of Traube, shaking with saline solutions, such as ammonium sulphate, by which a concentration of the fusel is obtained, is only then of any use when very large quantities of the salt are used. For instance, to concentrate the fusel from

a litre of alcohol containing 1 gram. of amylic alcohol into 100 c.c., it was found necessary to shake with no less than 15 litres of a saturated solution of ammonium sulphate. The experiments were therefore not continued.

#### TESTING OF VARIOUS SAMPLES OF PURIFIED SPIRITS.

Our process to increase the fusel by fractional distillation and then to estimate it quantitatively, is as yet only practicable in the case of spirits poor in fusel, for which it, however, possesses an undoubted advantage. From our experiments with pure spirits, and the same when mixed with a definite amount of fusel, one can see that intermediate fractions are obtained which give a constant chloroform increase. (We take it, of course, for granted a chloroform of the same quality is used.) Instead of only testing the last, or the two last fractions, it is always as well to test one of the earlier ones so as to have a better check on the analysis.

No. 1. *Sample*.—First-class potato spirit, *so-called* spirits of wine, from the later fractions of a distillation, containing 95.5 per cent. of alcohol. 1,000 c.c. were allowed to stand on 100 grams. of dry potash for two or three hours at the ordinary temperature and then fractioned. The boiling point remained constant at 78.7° until the last drops distilled over. The remaining potash was dissolved in water and 100 c.c. of this distilled off.

Last fraction from 100 c.c.—

Noticed volume  $V = 54.55$   $T = 14.9^{\circ} \text{C.}$

Volume at normal temperature  $V_{15} = 54.56$

Last but one fraction from 100 c.c.  $V = 54.50$   $T = 14.8^{\circ}$

$V_{15} = 54.52$

The increase in the chloroform volume is for both fractions a little less than with the spirit sent as pure. On the other hand the intermediate fraction of the last-named give a chloroform increase of .06, and its ninth fraction an increase of .02 c.c. As an increase of .01 c.c. means .0028 c.c. of amylic alcohol, .02 c.c., .0056 per cent. Allowing for the dilution up to 320 c.c., we get .01792 c.c., = .0017 per cent. by volume of amylic alcohol, a quantity so small that it may be put to experimental error and be disregarded.

No. 2.—A strong spirit, prepared by a new process from maize containing 95.65 per cent. of alcohol.

1,000 c.c. were distilled with 100 grammes of dry potash. The boiling point kept constant at 78.8° C. until the last fraction. The treatment was the same as in No. 1. The last fraction of 100 c.c.  $V = 54.55$ . Consequently the spirit must be considered free from fusel. The first fraction had a faint ethereal smell. On testing this first fraction  $V_{15} = 54.69$ .

The shaking out of the spirit without previous distillation gave

$V_{15} = 54.71$ .

After rectifying over KHO we got

$V_{15} = 54.48$

$V_{15} = 54.51$

showing here the necessity of rectifying over caustic potash.

---

\* Using the same chloroform in the small Hersfeld's apparatus  $V_{15} = 20.80$  c.c.,

No. 3.—Rectified corn brandy contained 95.2 per cent. of alcohol. 1,000 c.c. were distilled with 100 grams. of potash. The boiling point kept constantly at 78.7° C., and only reached 79.2° at the end of the distillation.

Last fraction 100 c.c.  $V = 54.49$ ;  $T = 14.9$

Corrected  $V_{15} = 54.50$

$V = 54.51$ ;  $T = 15.1$

Corrected  $V_{15} = 54.50$ .

100 c.c. of the last but one fraction  $V_{15} = 54.50$ .

The spirit is to be regarded as absolutely free from fusel, but did not, however, possess such a pure odour as the first, and gave after dilution, but without previous distillation,

$V = 54.71$ ;

and after rectifying over caustic potash

$V = 54.69$ .

So it seems this sample contained volatile impurities which were not removed by KHO.

The first portions of the distillate gave respectively

1.— $V_{15} = 54.80$

2.— $V_{15} = 54.72$ .

From these figures it is plain that the testing of the last fractions is the best plan in any case; better than testing the whole of the spirit, even after rectifying with caustic potash.

It seems that spirits often contain volatile impurities which interfere with the analysis even when the sample has been rectified over potash or caustic potash. These bodies will certainly cause a too high result with spirits, which, being rich in fusel, cannot first be distilled, but it is a question whether this error is at all considerable. Further experiments will have to decide this.

#### EXPERIMENTS WITH TRAUBE'S CAPILLARIMETER.

Some time ago we have, like Sell and Mayrhofer, pointed out that the estimation of fusel in brandies by this instrument is certainly easy of execution, but that the process was inferior in accuracy to the shaking-out process. At the same time as we did the other experiments, we carried out some more experiments with the capillari meter, as the spirits used could not contain any large quantity of ethereal oils. We used the instrument as described by us in the *Repert Anal Chemie*, 1886, p. 386, with micrometric screw, and first determined the radius of the capillaries with the aid of quicksilver. A measured column of the mercury was then weighed, and so the volume calculated. The radius was

$$r = V \frac{v}{\pi \cdot h} : \dots 1793$$

The height increase for 20 per cent. alcohol was 49.5 mm. at 15° C. in our apparatus. If temperature was over 15° C., .18 mm. had to be added for each degree. The instructions accompanying the apparatus were not correct, and it is, therefore, no matter of surprise that not much confidence is felt in the method. The figure for water is 83.5 at 20.2° C. Pure amylic alcohol was now mixed with alcohol and water in such

proportions that the liquid contained exactly 1 per cent. of fusel, and the specific quantity of the same exactly corresponded with a 20 per cent. ethylic alcohol. By diluting with a 20 per cent. pure alcohol, mixtures were obtained which contained from .1 up to 1 per cent. of fusel. The figure of each mixture was then determined. It amounted on an average to .78 mm. for every .1 per cent. of fusel, the increase being remarkably constant, and any slight differences were most likely due to experimental error. We, however, think that if the amount of fusel is large, the figure gets slightly less and believe it to be safer to take the figure as .80 when the quantity of fusel lies between .1 and .5, and to reckon .76 when between .5 and 1.0 per cent. This difference of .04 mm. has really no practical importance, as it is not possible to read off to less than .1 mm. In using the capillarmeter it must be noticed that the alcohol must not be allowed to stand in the open basin or beaker for hours, but that the reading ought to be made after say five minutes. Alcohol being volatile, its strength in the open dish rapidly alters, particularly in a warm room.

We have performed a great number of estimations of fusel, and agree that the apparatus, on account of its simplicity and convenience, is in many cases an excellent one for the sorting of spirits, but we stick to our previous opinion that when great accuracy is required, the shaking process is much safer and more accurate.

It would not be interesting to give here our numerous figures of the height increase, and will content ourselves with mentioning some more results of our fusel-concentrating process.

1.—5 c.c. of amylic alcohol were mixed with a 1,000 c.c. of a 96 per cent. spirit, and then fractionally distilled after addition of 100 grams. of potash. The last fraction, when made up to 20 per cent. strength, measured 482 c.c. The height increase compared with pure 20 per cent. alcohol was .75 mm., corresponding with .094 per cent. by volume of fusel, or .453 per cent. in 482 c.c. liquid. As the original mixture contained .5 c.c., or .05 per cent. of fusel, the loss during the distillation must have amounted to .0047 per cent.

2.—1.0 c.c. of amylic alcohol was mixed with 1,000 c.c. alcohol and 100 grams. of potash, and then fractioned. On testing the last in 100 c.c., .912 fusel was found, showing a loss of .0088 gram. or .088 per cent. by volume.

3.—1.5 c.c. amylic alcohol + 1,000 c.c. spirit + 100 grams. of potash were mixed and fractioned—

|               |             |
|---------------|-------------|
| Last fraction | .888        |
| „ but one     | .185        |
| „ „ two       | .185        |
|               | <hr/> 1.258 |

Therefore .242 gram. of fusel oil, or .0242 per cent. by volume, had past over with the first portions, and this confirms once more our idea that the process is only useful when the amount of fusel does not exceed .1 per cent.

The numbers just mentioned still want a correction. To dilute the fusel the same spirit was used as in the experiments with the shaking apparatus. This spirit was not altogether free from fusel, but contained (by that process) .19 c.c. fusel oil. To get approximately correct results, we must, of course, allow for this, and then we get the following figures:—

| 1 litre of spirit was mixed<br>with | Recovered<br>in shaking apparatus. | by capillarimeter. |
|-------------------------------------|------------------------------------|--------------------|
| ·5 c.c. fusel; last fractions       | ·31 c.c.                           | ·26 c.c.           |
| 1·0 c.c. „ „ „                      | ·91 c.c.                           | ·72 c.c.           |
| 1·5 c.c. „ 3 last fractions         | —                                  | 1·06 c.c.          |

## THE DETAILS OF OUR PRESENT PROCESS.

The estimation of the fusel by shaking with the chloroform must first of all be done in the ordinary way after distilling the spirit with caustic potash, in the fluid diluted up to 30 per cent. If the analysis should show a result exceeding ·15, the analyst must take this as practically accurate. If, however, less than ·15 per cent. is found, 1,000 c.c. of the spirit and 100 grams. (or more) of calcined potash are introduced into a large fraction apparatus, and after standing for a few hours it is distilled off. The first 500 c.c. may be collected together, but after this every 100 c.c. are separately collected. After everything is distilled over, the retort is allowed to cool, and 250 c.c. of water are introduced. 100 c.c. are now distilled off from a paraffin bath, and the distillate united with the last alcoholic fraction. Now every fraction must be diluted up to 30 per cent. strength and (the last one first) examined in the apparatus.

The dilution up to 30 per cent. by volume must be done with the greatest possible accuracy; at all events, the experimental error should not exceed ·1 per cent., which will already cause a chloroform increase of ·03 c.c. The best shaking apparatus is such a one which has room for 250 c.c. of the spirit and 50 c.c. of chloroform. The central narrow tube of the apparatus should hold 50—56 c.c., and be divided into ·05 of a c.c., and one should be able to judge ·01 of a c.c. The temperature during the measuring of the fluids and the reading off should be between 14·5—15·5° C. The correction for temperature is made by allowing ·01 c.c. for every 1° C. either adding or deducting the same.

To get truly comparable results in the analysis of different kinds of spirits, we recommend, not only to state the percentage of fusel as found, but also to calculate its proportion to the alcohol which the sample contains.

## DETERMINATION OF LITHIA IN MINERAL WATERS.

BY E. WALLER, PH.D.\*

PRACTICALLY, three methods are now available. 1. The phosphate method (Mayer's modification) (*Ann. Chem. u. Pharm.* 98, 193). 2. The amylalcohol method (Gooch, *Am. Chem. Jour.*, 9, 33). 3. The fluoride method (Carnot, *Bull. Soc. Chim.* [3] 1, 280).

Rammelsberg's method (*Pogg. Ann.*, 66, 79), somewhat similar in principle to that of Gooch, in that it depends upon the comparatively greater solubility of lithium chloride in an organic solvent, has been comparatively little used, on account of the difficulty and expense involved in obtaining the pure anhydrous alcohol and ether necessary for the process. Moreover the experiments of J. L. Smith (*Am. Jour. Sci.* [2] 16, 56), rearranged in convenient form for reference by Gooch do not indicate that it is very satisfactory in its application, even with the best of care. Some indirect processes, such as the weighing of mixed chlorides of sodium, potassium and lithium, and then

\* Journal of the American Chemical Society.

determining the chlorine and potassium (Bunsen, *Ann. Chem. u. Pharm.*, 122, 348), have been also proposed, but they are troublesome in execution, and likely to be unsatisfactory in result.

For all of these processes, it is necessary to obtain from some known quantity of the water, the alkalies as chlorides free from admixture with other bases, and in most cases, a considerable proportion of the sodium and potassium salts, which usually predominate largely over those of lithium, must be removed. To accomplish this the usual method may be followed, acidification with hydrochloric acid, evaporation, treatment with barium hydrate solution, removal of the excess of baryta by ammonium carbonate, driving off the ammonium salts, and extraction with alcohol or alcohol and ether, to take out the lithium chloride which is inevitably accompanied by some sodium and potassium chlorides. Throughout this treatment, the spectroscope must constantly be used to determine when the extraction or washing is complete, and these preliminary operations often prove very tedious. Some suggestions in this connection may be of value. The small platinum wires used to test the precipitates, solutions, etc., need critical examination. A wire which has been once used with lithium salts may perhaps be held in the flame until it will give no trace of colour to the flame, nor show the lithium line by the spectroscope, but on moistening with hydrochloric acid and inserting in the flame, the line will show almost as brightly and distinctly as if no lithium had been removed from it. Repeated scouring, immersion in acid and insertion in the flame, or long soaking in acid may be necessary to remove this trace of lithium from the wires. It has been found convenient to keep several wires dipping into a test tube partially filled with dilute hydrochloric acid, and to use them in succession, so that each wire shall have a tolerably long immersion in the acid, before being tested again, as a preliminary to using it for a test on a precipitate, etc.

Barium precipitates ( $\text{BaCO}_3$  and  $\text{BaSO}_4$ ) when formed in the presence of lithium compounds, carry down and retain perceptible quantities of lithia (by spectroscope test) with great persistency. The well-known tendency of the barium sulphate to drag other salts with it *seems* to be greater in the case of lithia than in that of other alkaline salts, although this may perhaps be due to the exceeding delicacy of the spectroscopic reaction. Precipitation in a rather dilute solution, and rather liberal washing is usually the most convenient course to pursue in the case of the precipitation of  $\text{BaSO}_4$  in presence of lithium salts. With  $\text{BaCO}_3$ , re-solution in  $\text{HCl}$ , and re-precipitation with ammonia and ammonium carbonate is most effective. If the proportion of lithium is large, re-solution and re-precipitation a third time may be advisable. The precipitate produced by barium hydrate, unless consisting largely of sulphate, does not give so much difficulty in the washing out of the lithia, except when it has been exposed for some time to the air of the laboratory containing  $\text{CO}_2$ .

A word further as to the decomposition of  $\text{LiCl}$  by heat. Direct quantitative estimations upon the subject were not made in this investigation, but the phenomena noted tend to confirm Mayer's remark that under the influence of heat in presence of water, lithium chloride has a tendency to exchange chlorine for oxygen.

A solution containing lithium chloride is evaporated to dryness with difficulty when placed on the water bath, and if it finally is made to *appear* dry after prolonged treat-

ment in this manner, more of the material is slow to re-dissolve in water (apparently because of the formation of lithium hydrate) than if the same solution is evaporated nearly to dryness and the moisture driven out by careful ignition over a naked flame.

Assuming in every case that one has obtained a concentrated aqueous solution from a known quantity of the water, containing all of the lithium and some of the potassium and sodium as chlorides, but no other bases, the phosphate method would be as follows :—

Add an excess of hydro-disodium phosphate, and then a moderate excess of pure sodium hydrate, evaporate to dryness, re-dissolve in water by the aid of a gentle heat, add an equal volume of strong ammonia, digest warm for some time, allow to stand for twelve hours, filter and wash with a mixture of equal volumes of ammonia and water, and finally ignite and weigh as  $\text{Li}_3\text{PO}_4$ . A second or third portion of precipitate may be recovered, by evaporating the filtrate and washings, adding ammonia and allowing to stand as before, filtering, etc. The chief difficulty with the accuracy of the process, consists in the practical impossibility of obtaining all the lithium as phosphate, free from any other alkaline salts. Too much washing will cause appreciable amounts of lithium phosphate to go into solution. Indeed, in my experience the filtrate and washings have always showed a decided lithia line in the spectroscope, from the start. On the other hand, too little washing leaves some alkaline salt along with the lithium phosphate—shown by its tendency to cake on ignition—but whether it cakes or not, lithium phosphate separated by this method when tested by the flame, almost invariably gives so strong a sodium flame, as practically to obscure the red of the lithium to the naked eye. Consequently it becomes to a considerable extent a matter of judgment, to decide when the washing is completed, and *then* the amount of lithium phosphate obtained is a compromise between the precipitate dissolved off by washing and alkaline salts left with it. However, by the aid of a little experience, the error can be usually brought within moderate limits, if the proportion of water which the chlorides represent is sufficiently large (ordinarily 10 to 20 litres). The use of such large quantities of water is naturally attended with more or less labour, in evaporation, removal of bases, etc., and is in itself objectionable aside from the sources of error inherent in the method of determination. This method has, however, until recently been practically the only one in general use.

The method of Gooch used by him in the examination of the waters of the Yellowstone Park (*Bull. U. S. Geol. Survey*, No. 47, also *Chem. News*, 59, 113, *et seq.*), may be described as follows :—

The concentrated solution of the alkaline chlorides should contain only about 0.2 gram. of salts in all. To this solution, in a casserole or dish, is added 30 to 50 c.c. of pure *anhydrous* amyl alcohol. The vessel is then heated on a sand bath over a low flame, so as to boil off the water through the amyl alcohol, leaving the undissolved salts adhering to the sides of the dish. The heat is kept up until the volume of amyl alcohol has been reduced to about 15 or 18 c.c. after cooling. A few drops of hydrochloric acid are added to restore to the form of chloride any lithium oxide or hydrate which may have been formed, and the heating is repeated for a short time. The amyl alcohol is then filtered through paper, or through a Gooch crucible, into a measuring cylinder, and its volume noted (usually 10 to 15 c.c.). In case the proportion of lithium is large the undissolved salts should be taken up with a little water, and the treatment repeated in



the same way as just described, the amount of amyl alcohol which has been heated with the chlorides being measured as before. The salts are then washed with cold amyl alcohol until no trace of lithium is perceptible in them by the spectroscope; the filtrate and washings are evaporated in a weighed platinum dish, and the chlorides converted into sulphates, ignited and weighed. From this weight, for every 10 c.c. of amyl alcohol which remained in contact with the chlorides after heating, the following deduction is made:—

When only sodium and lithium chlorides were present, 0.00050 gram.

" " potassium " " " " 0.00059 "

When both sodium and potassium, as well as lithium  
chlorides were present ... .. 0.00109 "

The cold amyl alcohol used for washing dissolves so little that it is needless to take it into account.

The relative solubilities of NaCl, KCl, and LiCl in amyl alcohol, as determined by Gooch, are essentially:—

|      |     |     |  |       |
|------|-----|-----|--|-------|
| NaCl | ... | ... | 1 in 30,000, or 0.0041 gram. in 100 c.c. |       |
| KCl  | ... | ... | 1 " 24,000, or 0.0051 "                  | 100 " |
| LiCl | ... | ..  | 1 " 15, or 6.60 "                        | 100 " |

Temperature seems to have but little influence upon the solubility of NaCl and KCl.

Pure amyl alcohol freed from water by boiling, if necessary, is indispensable.

Gooch's test experiments with mixtures of pure salts may be here quoted, arranged in a form slightly different from that given in his paper. The  $\text{Li}_2\text{SO}_4$  obtained was calculated back to LiCl in every case. The error is noticeably greater in the presence of potassium chloride.

| Ex. pt. No. | Conditions.         | Li Cl taken. | Errors in corrected weight of Li Cl found. |
|-------------|---------------------|--------------|--|
| (23)        | Na Cl only { Single | 0.1298 grm.  | 0.0002— grm.                               |
| (24)        | " " { Extr'n        | 0.1227 "     | 0.0002— "                                  |
| (32)        | " " { Double        | 0.1287 "     | 0.0007— "                                  |
| (33)        | " " { Extr'n        | 0.1347 "     | 0.0006+ "                                  |
| (26)        | KCl only { Single   | 0.1256 "     | 0.0008— "                                  |
| (27)        | " " { Extr'n        | 0.1287 "     | 0.0010 - "                                 |
| (34)        | " " { Double        | 0.1125 "     | 0.0003+ "                                  |
| (35)        | " " { Extr'n        | 0.1251 "     | 0.00011+ "                                 |

The average of these errors is 0.0001— with a range from 0.0010— to 0.0011 + or if we calculate to the equivalent in  $\text{LiHCO}_3$  from 0.0016--- to 0.00176+, a difference of 0.00376 gram.

The process has the advantage that the sodium and potassium chlorides are left in a condition for the determination of those bases, in which case, however, an allowance must be made for the small amounts dissolved by the amyl alcohol which was heated with the chlorides. One disadvantage of the process is to be found in the fumes of the amyl alcohol which, even in a well ventilated laboratory, is a source of great discomfort to most analysts.

The small amount of water, 100 to 200 c.c. that can be used for this process is advantageous, though for those accustomed to the use of the phosphate process, the amount seems hardly large enough to give a fair average, and to average on a larger amount requires the concentration of the LiCl by extraction with alcohol or alcohol and

ether. In some of the first trials made with the process, the amount of mixed chlorides experimented upon considerably exceeded 0.2 gram., probably nearly 1 gram., and in some cases more. This was because Prof. Gooch's paper seemed to imply that the operation might be reasonably expected to be successful, when applied to quantities ordinarily handled in analytical work. In the case of one water it did do so, but with another water, containing more lithia as well as alkaline salts, it was not. The removal of all the water in the manner described was a matter of extreme difficulty, and, curiously enough, a limit seemed to be reached, beyond which the  $\text{LiCl}$  was extracted, but slowly and with great difficulty. The results may prove interesting.

The alkaline salts from two equal quantities of a water, each lot amounting to between one and two grams., were treated as described :

|   |        |                                       |        |                          |
|---|--------|---------------------------------------|--------|--------------------------|
| Obtained from A . . . . .               | 0.2400 | gram. $\text{Li}_2\text{SO}_4$ from B | 0.2354 | $\text{Li}_2\text{SO}_4$ |
| Found in insoluble part. f. A . . . . . | 0.0974 | „ „ B                                 | 0.0943 | „                        |
| Total . . . . .                         | 0.3374 | „                                     | 0.3297 | „                        |

The control process used in this case was Carnot's fluoride method, which cannot, however, be regarded as absolutely free from imperfections. It is as follows : the mixed alkaline chlorides after, evaporation nearly to dryness, are extracted with a mixture of about equal volumes of alcohol (of 90 per cent. or over) and ether, so as to obtain the  $\text{LiCl}$  comparatively free from the others. It was found most convenient to add the alcohol ether mixture, and allow to stand for some time with frequent stirring, and then after standing over night to filter through a small filter, and wash with alcohol ; one extraction will often suffice. A second extraction may, however, be necessary, the work being of course controlled by the indications of the spectroscope. After evaporating off the alcohol and ether, the salts are dissolved in the least possible quantity of water, and filtered into a weighed platinum dish. The filtrate and washings should then be concentrated to small bulk (5 or 10 c.c.) and pure ammonium fluoride and ammonia added ; after thorough mixing the dish is set aside over night for the  $\text{LiF}$  to precipitate. The solution is then decanted through a small filter, and the precipitate is washed by decantation three or four times (5 to 7 c.c. at a time), with a solution consisting of the reagent mixed with 5 to 10 times its bulk of ammonia ; between the decantations the solution must be allowed to stand some little time with stirring. The bulk of filtrate and washing (30 to 50 c.c.) is noted, the filter paper and contents placed in the dish, sulphuric acid added, and heat applied until the paper has been incinerated, and the lithium converted to sulphate, in which form it is weighed. To this weight is added 0.0040 gram. for every 7 c.c. of filtrate and washings, and the result estimated as  $\text{Li}_2\text{SO}_4$  is calculated to  $\text{Li}$ ,  $\text{LiHCO}_3$ , etc., according to the requirements of the case.

Care is necessary in preparing the reagent, and wash liquor.

Carnot seems to have found that the ammonium fluoride ordinarily supplied for laboratory use is the only member of the combination liable to contain impurities which would interfere (chiefly fluosilicic acid, which might precipitate alkaline fluosilicates), but experiments have shown that ammonia, which has been standing for some time in contact with glass, will give a cloud (presumably ammonium fluosilicate) with a mixture of solutions of ammonium fluoride and ammonia after boiling and filtering clear. This solution, so long as it contains a fair amount of free ammonia, appears to be without action upon glass. It has been found advisable therefore to make up (and cork up) the reagent and washing solution some time beforehand, and to filter off such portions as

may be required at the time of using. Naturally, it is necessary to use for the final filtration, a filter paper which has been extracted with hydrofluoric acid. Schleicher and Schull's papers were found satisfactory in this connection. Carnot also recommends that the resulting  $\text{Li}_2\text{SO}_4$  should be dissolved in 40 to 50 c.c. of water, and a test made for the presence of magnesium, which may have remained with the alkaline chlorides. If any is found to be present, it must be determined as phosphate and a correction made accordingly.

In connection with this process it was observed that lithium sulphate ignited in contact with the carbon of the filter paper, is especially prone to reduce to sulphide, and especial caution is necessary at this stage of the operation. The sulphide, when heated in contact with the platinum, attacks it in a very marked manner.

The process seems to be very good, although not rapid.

Its tendency is to yield results a little high, apparently because the allowance for solubility is usually larger than the actual amounts of precipitate dissolved. Test analysis tended to show also that unless the amounts of potassium and sodium chlorides present with the lithia are kept within narrow limits, the results will be high.

Unfortunately a number of the tests and comparison experiments with these methods have not yet been completed, and will have to be deferred to a second communication.

In order to test these methods upon water containing lithia, samples of several of the best known and widely advertised waters were purchased and submitted to examination.

The results were somewhat surprising, and shewed unquestionably that either the original analyses, on the strength of which those waters are now sold, were erroneous, on account of imperfection in the methods used, or, what is more probable, that the proportions of lithium in those waters are liable to great fluctuations.

The results given were chiefly obtained by Carnot's fluoride method, but were in several cases confirmed by the use of other methods. The most scrupulous care was exercised to be sure of obtaining *all* of the lithium in the waters under examination, the spectroscopic indications having been used at every stage of the process.

In the Farmville Lithia Water, purchased at the office of the company, no lithium could be detected by the spectroscope on moderate amounts of water. On evaporating eight litres of the water, and treating in the manner described for the concentration of the lithia into a solution of small bulk, a lithia line was obtained in the spectroscope, but the amount was found to be too small to admit of a quantitative estimation. The experiment was repeated with ten litres of the water, with essentially the same result.

With the Buffalo Lithia Water the reaction for lithium was more distinct, when considerable quantities of the water were concentrated. From twenty litres of the water was obtained lithium sulphate corresponding to 0.0185 part  $\text{LiHCO}_3$  per 100,000.

In the Londonderry water, the lithia reaction could be obtained without great difficulty. Analysis of the water purchased by myself showed a little over four parts per 100,000. The company puts up some of the water in half-gallon bottles not charged with  $\text{CO}_2$ , and also some in pint bottles (called in their circulars "sulpho-carbonated"), which is charged with  $\text{CO}_2$ , and has also received the addition of some salts. The amounts of salts added appears to be somewhat irregular. For instance, the following results were obtained (results given in parts per 100,000):

|  | Total solids. | Loss on ign. |
|--|---------------|--------------|
| Londonderry, half-gallon bottles (aver.) .. .. | 37.35         | 2.25         |
| "    pint bottle, A .. ..                      | 149.1         | 4.9          |
| "    "    B .. ..                              | 104.2         | 4.5          |
| Average of eleven others .. ..                 | 224.7         | 6.4          |

The variations in the eleven bottles were 221·3 to 231·4, for total solids. The proportion of lithium was essentially the same as for the still water.

I was told that several lots of water, purporting to come from these springs, had at times appeared on the market in which no lithia could be detected. As I learned that Dr. Endemann had obtained some water of that kind, I requested him to send me a bottle. He complied, and although the bottle bore all the labels and marks similar to those purchased by myself, no lithia could be detected in it. The water contained 5·2 parts total solids per 100,000. I have heard of others who had similar experiences.

I naturally desired to obtain samples of these water direct from the springs, taken by some one whom I knew to be disinterested. Attempts thus far have been unsuccessful. In the case of the Londonderry springs, all access is denied to visitors, and applications for water are referred to the bottling establishment in Nashua.

Of all the waters examined, purporting to be natural, the Saratoga Hathorn proved to be the strongest in lithia. The result of tests on this water are not at present in such form that they can here be recorded, but it suffices to say that the water contains fully as much as the analyses call for (twelve to fourteen parts  $\text{LiHCO}_3$  per 100,000, corresponding to seven or eight grains per U. S. gallon).

Tests were also made on the waters manufactured and sold by Carl H. Schultz as containing lithia. They were found to contain a little more lithia than claimed. E. g., the formula on his "Vichy with Lithia," called for an amount corresponding to about fifty-seven parts  $\text{LiHCO}_3$  per 100,000. The analyses showed sixty to sixty-two parts.

The results enumerated may be thus tabulated :

| Designation of Water, etc.           | Total Solids<br>Per 100,000. | Loss on Ign. | Non-Volatile. | Use for<br>Determination. | $\text{LiHCO}_3$ |                    |                   |
|--------------------------------------|------------------------------|--------------|---------------|---------------------------|------------------|--------------------|-------------------|
|                                      |                              |              |               |                           | Per 100,000      | Grs.<br>U. S. Gal. | Grs.<br>Imp. Gal. |
| Farmville Lithia, half-gal. bottles  | 16·4                         | 1·1          | 15·3          | 8-L                       | traces.          |                    |                   |
| " " " "                              | ....                         | ....         | ....          | 10-L                      | traces.          |                    |                   |
| Buffalo Lithia, half-gal. bottles..  | 93·2                         | 6·5          | 88·7          | 20-L                      | 0·0185           | 0·011              | 0·013             |
| " " " "                              | ....                         | ....         | ....          | 20-L                      | 0·0135           | 0·008              | 0·009             |
| Londonderry Lithia, h'lf-gal. bot's. | 37·35                        | 2·25         | 35·1          | 10-L                      | 4·171            | 2·432              | 2·920             |
| " " " "                              | ....                         | ....         | ....          | 10-L                      | 4·075            | 2·376              | 2·852             |
| " " " "                              | ....                         | ....         | ....          | 2-L                       | 4·130            | 2·408              | 2·891             |
| " " pts. (c'h'g'd $\text{CO}_2$ )    | ....                         | ....         | ....          | 2-L                       | 4·129            | 2·407              | 2·890             |
| " " " "                              | ....                         | ....         | ....          | 4-L                       | 4·074            | 2·376              | 2·851             |
| " " (half-gal. Dr. E.)               | 5·1                          | 1·           | 4·1           | 1-L                       | none             |                    |                   |

## THE USES OF HYDROGEN DIOXIDE IN QUANTITATIVE ANALYSIS, AND THE IMPORTANT METHODS FOR DETERMINING HYDROGEN DIOXIDE.

By C. H. JONES.\*

THE more important applications of hydrogen dioxide for quantitative purposes are given below.

Classen and Bauer† found that hydrogen dioxide can be used advantageously in

\* *American Chemical Journal.*

† *Ber. d. deutsch. chem. Gesell.* 16, 1061.

the determination of hydrochloric, hydrobromic and hydriodic acids in the presence of sulphuretted hydrogen. The latter is oxidised to sulphuric acid, and the chlorine, bromine and iodine are then determined in the usual manner.

The oxidation of sulphur to sulphuric acid by hydrogen dioxide is also employed to separate arsenic, antimony, zinc, copper and cobalt from the sulphur in their sulphides.

The sulphur can be liberated as sulphuretted hydrogen and oxidised by hydrogen dioxide. They employed this method in the determination of antimony trisulphide, antimony pentasulphide, tin, cadmium, and iron sulphides. It was found that hydrogen dioxide will also readily oxidise sulphur dioxide. This reaction is therefore employed to oxidise barium and sodium sulphites and sodium hyposulphite to sulphates.

P. Ebell \* determined lead dioxide by hydrogen dioxide in two ways. He used a known amount of the hydrogen dioxide, allowed it to decompose the lead dioxide, and then titrated the excess with potassium permanganate. He also effected the same decomposition, and measured the volume of the resulting gas. He recommends the former method. The latter method gave results which were too low as compared with those obtained by other methods.

G. Lunge † described a method for determining permanganate and manganese dioxide by means of an excess of hydrogen dioxide and sulphuric acid. The oxygen evolved was collected and measured, half coming from the manganese dioxide and half from the hydrogen dioxide.

The same author proposed later a method for determining the available chlorine in bleaching powder by means of an excess of hydrogen dioxide, half of the hydrogen evolved coming from the bleaching powder and half from the dioxide. But the volume of the oxygen set free is just equal to the total volume of the available chlorine in the bleaching powder.

A. Carnot ‡ determined chromic acid by hydrogen dioxide. The slightly acidulated bichromate solution was titrated with very dilute hydrogen dioxide, which was then standardised by means of pure bichromate. The end of the titration is shown by the absence of the blue colour when the dioxide is dropped into the chromic acid solution.

G. Lunge § recently recommended the slightly modified nitrometer for standardising potassium permanganate, and for determining bleaching powder and manganese dioxide by hydrogen dioxide and sulphuric acid.

Some of the above decompositions have been employed for the determination of the dioxide itself. These and other important methods for determining hydrogen dioxide will be briefly considered.

Barium dioxide was determined by Brodie || by treating it with hydrochloric or acetic acid in the presence of finely divided platinum or of animal charcoal, which decomposes the hydrogen dioxide catalytically. The apparatus, including the materials used, was weighed and the acid admitted to the barium dioxide. Decomposition having taken place, the apparatus was again weighed. The loss in weight equals the weight of the oxygen evolved.

In water solution, hydrogen dioxide has been determined by Schönbein. ¶ He acidified the solution with sulphuric acid in order to secure the complete reduction of the permanganate. The solution thus acidified was titrated with standard potassium permanganate until the first traces of colour appeared.

\* Rep. anal. Chem. 6, 141-43.

† Compt. rend. 107, 948.

‡ Phil. Trans. 1850, 2, 779.

§ Ber. d. deutsch. chem. Gesell. 18, 1872.

¶ Jour. Soc. Chem. Indst., January, 1890, 21.

|| Jour. für. prakt. Chem. 79, 78.

Another application of this same reaction has been proposed by F. Hamel.\* He treated the dioxide with a permanganate solution, collected and measured the oxygen evolved. At the same time he standardised his permanganate solution for further use.

Instead of potassium permanganate, A. Riche † employed manganese dioxide and sulphuric acid for determining hydrogen dioxide. The oxygen liberated was collected and measured. Lead dioxide is also used for the same purpose.

A method has been proposed by A. Houzeau ‡ which is based on the following reaction in acid solution:  $\text{H}_2\text{O}_2 + 2\text{KI} = 2\text{KOH} + \text{I}_2$ . A measured amount of standard acid was introduced into the neutral solution of the hydrogen dioxide to be determined. A small excess of potassium iodide was then added. The iodine liberated was boiled off and the excess of acid titrated with standard alkali.

Bertrand § used the above reaction to determine barium dioxide and hydrogen dioxide. Instead of driving off the iodine and titrating the excess of acid, he titrated the liberated iodine with a standard solution of sodium hyposulphite.

For the detection and determination of small quantities of hydrogen dioxide, Schöne || makes use of the decomposition of potassium iodide by the dioxide in neutral solution, and the detection of the free iodine by means of starch paste. He states that this method will detect 0.00008 gram. in a litre. When there is more dioxide present than 0.001 gram. in a litre, the method is not accurate, since the colour does not change in the same ratio as the substance. A milligram. and two-tenths to a litre give about the same colour as a gram. The minimum limit of accuracy is 0.0008 gram. and the maximum 0.001 gram. of the dioxide to the litre.

G. Lunge ¶ reversed his method for determining bleaching powder by hydrogen dioxide, and determined the dioxide by means of an excess of bleaching powder. The volume of the oxygen set free was measured, half coming from the bleaching powder, half from the dioxide.

Potassium bichromate has been used by Wilfart \*\* for an approximate determination of hydrogen dioxide. The dioxide was treated with dichromate and sulphuric acid, and the liberated oxygen measured.

A. Carnot †† titrated the dioxide with a standard solution of potassium bichromate in the presence of a little hydrochloric or sulphuric acid. Carnot states that this method is not as reliable as the permanganate method.

Attention is called to a piece of apparatus recommended by Maurice de Thierry ‡‡ for determining hydrogen dioxide.

Some work which I have done in this laboratory shows that the applications of hydrogen dioxide to quantitative analysis can be extended by the use of nitric acid instead of sulphuric. This works more satisfactorily where the formation of insoluble sulphates is involved. Thus, minium and lead peroxide yield thoroughly satisfactory results when treated with nitric acid and hydrogen peroxide. The commercial hydrogen dioxide should in all cases be diluted three or four times to prevent decomposition on standing.

For the determination of minium, an excess of the diluted dioxide and dilute nitric acid are placed in a 200 c.c. Erlenmeyer flask. About a gram. of minium is weighed in a weighing tube of convenient size, which is then placed upright in the flask. The flask is connected with a Hempel's burette or a Lunge nitrometer. The gas volume, after adjustment of pressure, is read. The weighing tube containing the minium is then over-

\* Compt. rend. 76, 1023.

† Compt. rend. 66, 44.

‡ Zeit. für anal. Chem. 18, 154.

\*\* Zeit. für anal. Chem. 1888, 417.

† Jour. pharm. Chim. [5] 13, 249-56.

§ Bull. Soc. Chim. d. Paris 33, 148.

¶ Ber. d. deutsch. chem. Ges. 19, 868.

‡‡ Compt. rend. 107, 948.

‡‡ Jour. pharm. Chim. [5] 12, 501-2.

turned into the mixture of nitric acid and hydrogen dioxide. In a few minutes the decomposition is complete. The increase in volume is ascertained and reduced to standard conditions of temperature and pressure. Half of the oxygen comes from the minium and half from the hydrogen dioxide. The water in the burette should be made slightly alkaline with sodium or potassium hydroxide, to remove any traces of carbon dioxide which may come from the action of nitric acid on impurities in the minium. The results obtained, expressed in percentages of oxygen were :

|                |        |
|----------------|--------|
| Oxygen.        |        |
| 2.40 per cent. |        |
| 2.39           |        |
| 2.36           |        |
| <hr/>          |        |
| Average,       | 2.38 + |

To test the above results, portions of the same specimen of minium were heated in a vacuum, the oxygen pumped away as rapidly as it was set free, and measured after removal of carbon dioxide. Under these conditions the minium passed completely into lead oxide. The results were :

|                |        |
|----------------|--------|
| Oxygen.        |        |
| 2.37 per cent. |        |
| 2.36           |        |
| 2.36           |        |
| <hr/>          |        |
| Average,       | 2.36 + |

We attempted to determine the oxygen in the same specimen of minium by heating it in hard glass tubes attached to a Hempel's burette and measuring the oxygen evolved. Platinum gauze was placed in the tube to facilitate the distribution of heat. The results, expressed in percentages of oxygen, were :

|                |        |
|----------------|--------|
| Oxygen.        |        |
| 2.19 per cent. |        |
| 2.21           |        |
| 2.22           |        |
| 2.26           |        |
| 2.20           |        |
| <hr/>          |        |
| Average,       | 2.21 + |

As will be seen, the results are too low. This is to be attributed to a partial recombination of the lead oxide and oxygen during cooling.

The method \* sometimes employed for determining lead dioxide by heating in the air and ascertaining the loss in weight is subject to the same source of error.

The determination of lead dioxide was carried out in all respects like that of minium. The specimen should be finely pulverised, and a half-gram. or less used in a determination. The results with hydrogen peroxide and nitric acid, expressed in percentages of oxygen evolved, were :

|                |        |
|----------------|--------|
| Oxygen.        |        |
| 5.43 per cent. |        |
| 5.43           |        |
| 5.42           |        |
| <hr/>          |        |
| Average,       | 5.42 + |

Determinations of the same specimen by heating in a vacuum were carried out as in the former case. More carbon dioxide was found here than in the minium. .3 per cent. of carbon dioxide was removed from the oxygen. The results, expressed in percentages of oxygen, were :

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\* Zeits. für anal. Chem. 14, 348.

Oxygen.  
5.45 per cent.  
5.43

Average, 5.44

The determination of manganese dioxide by hydrogen dioxide and sulphuric acid has been made by Lunge as above mentioned. But we find that nitric acid is preferable, as will appear below.

A specimen of manganese dioxide was ground and dried. Two determinations were made by Lunge's method, with the following results :

Oxygen.  
13.13 per cent.  
13.14

Average, 13.13 +

Two determinations of oxygen in the same specimen, made with the use of dilute nitric instead of sulphuric acid, gave :

Oxygen.  
13.17 per cent.  
13.24

Average, 13.20 +

The slightly higher results in the second case are, perhaps, due to the presence of ferrous iron in the ore, which are oxidised by the nitric acid, and loss in available oxygen avoided. To test this we added equal amounts of a ferrous salt to weighed portions of the manganese dioxide, and determined the oxygen by sulphuric and nitric acids respectively. The results obtained when sulphuric acid was used were slightly lower, while when nitric acid was employed they were practically constant. This tends to confirm the above idea.

That hydrogen dioxide can be determined by minium and nitric acid, or lead dioxide and nitric acid, will be seen from the following results. The specimen was first determined by calcium hypochlorite. The results are expressed in litres of oxygen obtained from one litre of hydrogen dioxide.

Results when calcium hypochlorite was used.

Oxygen.  
5.890  
5.890  
5.880

Average, 5.8866 +

Results when minium and nitric acid were employed :

Oxygen.  
5.900  
5.910  
5.910

Average, 5.9066 +

Results from the decomposition by means of lead dioxide and nitric acid :

Oxygen.  
5.910  
5.900  
5.910

Average, 5.9066 +

*Chemical Laboratory, John Hopkins University.*



## LAW NOTES. •

## SALICYLIC ACID.—IMPORTANT STATEMENT BY PROFESSOR CHARTERIS.

In the County Buildings, Glasgow, October 16th, David Reid, chemist, 156, New City Road, was charged before Sheriff Balfour, at the instance of Mr. Peter Wile, sanitary inspector, with having, on 3rd July, sold to Inspector Armstrong one ounce of salicylic acid, which contained  $2\frac{1}{2}$  per cent. of cresotic acid. He pleaded not guilty.

Mr. Angus Campbell, writer, who appeared for the respondent, said that what he sold was commercially known as salicylic acid, and was made under the pharmacopœia formula which was in general use. Cresotic acid was almost inseparable from salicylic acid, except under the formula recently adopted by Professor Charteris, who had discovered means of still further purifying the drug.

Mr. R. G. Ross, writer, who prosecuted, said that the object of the sanitary authorities was not to press for a penalty, or even for a conviction, but to let the public know what they were getting.

Professor Charteris, who was the first witness, said that he was professor of materia medica in Glasgow University. Salicylic was principally used for the treatment of acute rheumatism. It was taken inwardly. There were two kinds of salicylic acid—natural, which was obtained from salicin and oil of winter-green, and artificial, which was obtained from carbolic acid. He was at the Royal Infirmary in 1880, and used artificial salicylic acid for rheumatism. He found that when it was prescribed for two days in the ordinary dose it created bad symptoms, such as delirium, restlessness, and a desire to get out of bed. He tried natural salicylic acid, and it had no bad results. He then stopped the use of the artificial acid altogether, and since 1880 had used only the natural acid. He had known of serious results from the use of the artificial acid. During the summer of last year he made experimental researches, testing the natural and the artificial acid. The latter was a powdery substance like quinine, while the natural acid had clear, well-defined crystals, something like strychnine. He found that the artificial acid in ten-grain doses was fatal. He applied it to a rabbit weighing  $2\frac{1}{2}$  lbs., and it caused convulsions and death. He applied the same quantity of the natural acid to another rabbit, and there were no bad results. He experimented on the artificial acid with a view to taking out the impurities. The detection of the latter was mainly due to Mr. Henderson. The impurities were probably some form of impure salicylic acid and cresotic acid. The impurities taken out of the artificial acid had the appearance of a brown, dun powder. He made experiments with these impurities, and found that one grain of this brown powder was fatal to a rabbit weighing  $2\frac{1}{2}$  lbs. It was very simple to extract the impurities. Cresotic acid was poisonous. The impurities taken from the artificial salicylic acid were distinctly poisonous. His experience, fortified by that of other physicians, was that it was dangerous to the public to use artificial salicylic acid. In rheumatism it was necessary to give large and repeated doses, and these caused such symptoms as delirium and restlessness. These symptoms he accounted for by the impurities which were in the artificial salicylic acid. The natural acid cost four or five times the price of the artificial. Purified artificial salicylic acid cost 10d. and unpurified 9d. Kolbe's patent, by which the artificial acid was made, expired two years ago.

Cross-examined by Mr. Campbell: He scarcely thought that there were differences of opinion as to the result of using artificial salicylic acid. According to the pharmacopœia the melting point of salicylic acid was about 155 Centigrade. The article discovered by Kolbe was in almost constant use from the date of the patent in 1874 downwards. Kolbe's was the article known as artificial salicylic acid, and under the patent the discoverer had a monopoly of the manufacture. Since the expiry of patent chemists and druggists had, he presumed, dealt in the article manufactured under the Kolbe specification. The presence of  $2\frac{1}{2}$  per cent. of cresotic acid would not be a usual quantity, and there might probably be more. If "salicylic acid" were put in a prescription the chemist would supply the cheaper kind, but if witness wanted the other he would add the word "natural." The pharmacopœia recognised, but only vaguely, the natural acid as distinct from the artificial. When witness wanted the natural acid he always expressly said so, but he did not know if that was universally done. According to the formula in use down to witness's discovery he did not think that artificial salicylic acid could be got without the impurities. The natural article was made from salicin or else from oil of wintergreen. For one ounce of the natural acid forty or fifty ounces of the artificial were sold.

Dr. John Clark, City Analyst, stated that he examined the sample of acid bought from Mr. Reid, and found it to contain  $2\frac{1}{2}$  per cent. of cresotic acid. The melting point of the pure acid was 156·8, and the pharmacopœia gave it as about 155. The melting point of the sample was 154·7, and that was an indication of impurity. It had been assumed in this case that all the artificial salicylic acid produced under Kolbe's patent contained cresotic acid. That, however, altogether depended upon the purity or quality of the carbolic acid or phenol from which it was made. The presence of the cresotic acid in the salicylic acid was due to the impurity of the carbolic acid from which it was made. Fischer, in examining a number of commercial samples of salicylic acid made by Kolbe's process found no impurity in several of them.

By Mr. Campbell: Witness had examined other three samples of salicylic acid made by Kolbe's process, and in these there were only faint traces of impurities.

Mr. Ross said that after what had taken place he would withdraw the case.

The Sheriff said that notwithstanding the complaint having been withdrawn it had been a most useful prosecution, as it showed to the profession and the public the results of Professor Charteris's valuable discovery.

Mr. Campbell said that his client and these associated with him desired to the fullest degree to avail themselves of the discovery by Professor Charteris.

# THE ANALYST.

DECEMBER, 1890.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL meeting of the Society was held at Burlington House on Wednesday, 12th ult., the President, Mr. Adams, in the chair.

The minutes of the June meeting were read and confirmed.

The following gentlemen were declared duly elected as members:—G. A. Milne, F.C.S., Norton; Malton Hugh Barclay, F.C.S., Workington; Edgar Richards, F.C.S., Chemist to the American Inland Revenue.

The following gentlemen were proposed for election:—As members, J. J. Beringer, F.I.C., F.C.S., Analyst for Cornwall; Dr. Readman, Analytical Chemist. As associate, Mr. Gilbard, Assistant to Mr. Dyer, Edinburgh.

The following papers were read:—

"On Food Preservatives."—By OTTO HEHNER.

"On the Adulteration of Food with Boracic Acid."—By CHARLES E. CASSAL.

"On the Detection and Estimation of Boracic Acid in Milk and Cream."—By CHARLES E. CASSAL.

"On the Detection of Methylated Spirits, in Tinctures, Spirits, or other Compounds."—By DR. ASHBY.

The next meeting will be held at Burlington House on Wednesday, 10th December, 1890.

## ON THE USE OF FOOD PRESERVATIVES.

BY OTTO HEHNER.

(Read at Meeting, November, 1890.)

A FEW weeks ago a milk-seller was summoned before one of the Metropolitan police magistrates for selling milk which was partially deprived of cream, and which, in the



To preserve fresh fish about 2 grams. of boric acid are used to each kilo of fish.

Salicylic acid has not, I believe, ever been largely used in this country as a food preserver. It answers but very badly in the case of milk and butter, and its use is now chiefly confined to foreign fermented beverages. As to the quantity one gram. per litre was frequently used when salicylic acid had reached its height of popularity. When in course of time objections against its use were not only heard, but resulted in prohibitive legislation in many countries, 5 grams. were declared to be sufficient by its advocates to keep 100 litres of Bavarian beer for home consumption, and 20 grams. for export (E. Prior, *Deutsche Mediz. Wochenschrift*, vol. 13, p. 38).

If we now enter into the question as to the physiological effect of the preservatives mentioned, we at once meet with the most diametrically expressed opinions. Whilst inventors introduce every antiseptic as absolutely harmless, and quote experiments by which it is shown that large and continued doses of antiseptic were administered without evil effects, other enquirers come to absolutely different conclusions. Literature teems with arguments in favour of and against some of these substances, and it must, I think, be conceded that direct and palpably injurious effects on healthy individuals have not been traced to any of the antiseptics herein considered. But when so much is conceded, a wide field for discussion yet remains.

On the one hand it must be recognised that to prevent waste of good human food by avoiding or retarding, its decomposition is a meritorious achievement, and one upon which the thought of the scientific man cannot be too much concentrated. Yet it must be allowed that the indiscriminate addition of chemical substances which exert a poisonous action on bacterial and other organisms cannot be safely left in the hands of more or less ignorant vendors of articles of food, even if no directly poisonous or injurious action can be traced upon an healthy adult by their use. It is evident that substances which interfere with the growth of fungoid organisms like bacteria or yeast cells, must have some action upon the complicated human animal; and even if exuberant health and abundant gastric secretions may be capable many times to overwhelm the effect of the antiseptic, the effect itself must remain and detract from the efficiency of the human organism. It is inconceivable that the protoplasm of a bacteria be vitally affected by a substance which at the same time be utterly inert upon human protoplasm. The effect is evidently a question of quantity. The absolute quantity may not be sufficient to show itself palpably upon a body weighing, say, 1½ cwt., but it must be there all the same.

Well does the Comité Consultatif d'Hygiène Publique of France report in reference to the use of benzoic acid in articles of food that all antiseptics are injurious to natural digestion, because the addition of antiseptics of any kind is irrational as far as assimilation is concerned, and may be injurious to the normal action of the organs of digestion.

In times gone by, when the causes of the decomposition of food were not understood, the discovery of a preservative was doubtless an achievement; but now, when we not only know these causes, but can prevent decomposition indefinitely by exclusion of germs, or by cold, without the addition of any kind of foreign material, we surely should make an attempt to discriminate between processes of preservation. If preservation could not be effected without the addition of some foreign material, the benefit to

mankind of preventing good food substance from decomposition would doubtless be greater than the slight physiological evil effect of the antiseptic itself. But as preservation of any article of food is possible without addition of chemicals, it seems to me that the time has come for public analysts generally to set their faces against the present practice of allowing the addition of any antiseptic which the dealer in food may choose to make.

Isolated action, such as was undertaken by the public analyst to whom I referred in the opening of this paper, appears to me to be most inadvisable, as we would surely have to witness the deplorable spectacle of seeing one analyst giving his opinion against his fellow analyst in a perfectly contrary sense to the destruction of all chance of future legal definition. Of course, it may be that the policy of *laissez-faire* which has hitherto been adopted may commend itself, but if we consider that almost every country in the world has taken this matter up and restricted or prohibited the use of antiseptics in food, whilst England, the country in which food laws were first passed, has done absolutely nothing, it will be admitted that the time is at least ripe for discussion of the subject.

France was the first to raise objections against the use of preservatives. Most of the beer consumed in France used to be imported from Germany. When it was discovered that such beer almost invariably contained salicylic acid, a vigorous agitation, in the interest of French home brewers, commenced. Finally, the Paris Court of Appeal decided that the addition of salicylic acid was to be considered an adulteration, and to the prejudice of the purchaser. The addition was declared to be not harmless, it having been shown that salicylated ales were a source of danger to the community, that salicylic acid was a drug, the use of which had to be ordered by a medical man, and could not be left with the trader. This judgment was based upon a Report of the Commission of the Academie de Medicine of Paris on the Action of Salicylic Acid on Food. The Commission reported on numerous cases in which the preservation of articles of food by salicylic acid has produced serious results, and is of opinion that it is proved that small but continued doses of salicylic acid or salicylates, may produce serious gastric disturbances, especially with old persons and such who suffer from affections of the liver or organs of digestion. For these reasons the addition of salicylic acid, or salts, should not be allowed to articles of food.

What was originally probably a trade protectionist movement soon became a general opinion. The indiscriminate use of antiseptics should not be allowed, and one State after another passed laws forbidding the addition of preservatives to food, in some cases antiseptics generally, in others specified substances only.

Thus, by order of the Municipal Council of Buenos Ayres of January 5th, 1887, the sale of beer containing salicylic acid was prohibited after March 31st, 1888. Between these two dates the quantity of salicylic acid had to be stated, and was not to exceed .05 grm. per litre. Other South American States followed. On July 1st, 1887, the town of Milan passed a similar law, referring to the prohibition of salicylic acid in beer, wine, and other articles of food; whilst from July 6th, 1887, the police of Berlin prohibited the addition of any kind of preservative whatever to milk. The town of Schwerin (Mecklenburg) followed suit.

In 1888 the Dutch Government caused an enquiry to be made into the use of salicylic acid in beer, and, as a result, all addition of salicylic acid to food was prohibited. The Italian Ministry, by order of November 29th, 1887, declared the addition of all substances to wine, which were not naturally contained in wine, to be an adulteration; on January 30th, 1888, the Spanish Government followed with an absolute prohibition of antiseptics in wine, and the Austrian with that of salicylic acid.

In Germany, lastly, a distinction is made between salicylic acid added during mashing, to check the growth of the acid-producing organisms, such an addition at that stage of brewing being allowed, not any of the acid, or only traces of it, being said to remain in the beer, and between the subsequent addition of salicylic and fully fermented beer, which is prohibited.

When salicylic acid had thus been virtually suppressed, other antiseptics came into vogue. Thus, in France, the use of benzoates became frequent, partly on account of the greater power of these compounds, partly because they are more difficult to trace and detect than salicylic acid. In Germany sulphites and borates were more largely employed, and numerous preparations containing these as active ingredients were thrown upon the public. Thus, according to Polenske (*Arbeiten des Kais. Gesundheitsamts*, 1870, VI., 119), the following articles have been advertised in Germany:—

Sozolith, containing 39·7 per cent. sulphurous acid, as sodium salt.

Australian Meat Preservative, consisting of sulphites.

Berlinite, borax, with a little boric acid and nitrate of potash.

Chinese Preservative Powder, boric acid, with sodium chloride and sulphate.

Brockmann's Salt, borax, boric acid, sodium chloride, and potassium nitrate.

Australian Salt, borax.

Barmerite, boric acid and salt.

Magdeburg Preservative Salt, borax, boric acid, and salt.

Heydrich's Salt, sodium chloride, potassium nitrate, and boric acid.

Again, as in the case of salicylic acid in previous years, long discussions arose as to the physiological activity of these substances. Liebreich contended that boric acid was perfectly harmless, but others have been able to trace distinct physiological effects to its administration; whilst, at their meeting at Speier, on Sept. 10th, 1889, the Society of Bavarian Analytical Chemists discussed the use of boric acid as an antiseptic, and came to the conclusion that it was objectionable from a sanitary point of view.

In England we have done nothing, absolutely nothing. On the contrary, the use of antiseptics has been virtually sanctioned in brewing. The law 48 and 49 Vict., Cap. 51, declares that a brewer of beer shall not add any matter or thing thereto *except* finings, or other matter or thing sanctioned by the Commissioners of Inland Revenue.

The use of antiseptics, notably bi-sulphite of lime, which is here chiefly used in beer, is therefore distinctly conditional upon the sanction of the Inland Revenue Commissioners; and the same would be the case in other articles of food, since the chemists of the Inland Revenue Commissioners are referees for cases under the Food and Drugs Act. Bi-sulphite of lime being freely used in breweries, with the knowledge of Excise officers, a gentleman wrote to the Board to know if the employment of bi-sulphite of lime and salicylic acid were sanctioned. The reply, which I have seen myself, was that "The

Board do not sanction their use unless they interfere with the Revenue, leaving the responsibility for their use with the brewers."

Surely a remarkable and undignified position to take up. The Act of Parliament says: You shall add nothing to beer, except with the sanction of certain authorities. These authorities say, we leave these matters to the brewers. If the authorities of Buenos Ayres, or of Mecklenburg-Schwerin, were capable of coming to a conclusion, surely it might be reasonably hoped and expected, that the authorities of Somerset House would not remain behind. We public analysts have done no better. The Sale of Food and Drugs Act, par. 6, allows to be added to food any matter or ingredient not injurious to health, if the same is required for the production or preparation thereof as an article of commerce in a state fit for carriage or consumption. No one, surely, can contend that preservatives are necessary for the production or preparation of milk, butter, beer, wine, etc., in a state fit for carriage or consumption, for the great majority of the samples analysed are free from antiseptics. Good milk, fresh butter, sound beer, can be made and sold without antiseptics. As a matter of fact, they have been so sold for centuries, until sham science came in and taught the dirty and the careless producer how to evade the natural punishment of dirt and mismanagement. Antiseptics are convenient to such producers, but they are not *required*. Hence we have no option but to consider them as adulterations.

We might, no doubt, some time longer, as in the past, wink at the use of all preservatives without restriction as to quality or quantity; but we shall, sooner or later, have to answer for our apathy to the public. We might agree between ourselves what limits we would allow, beyond which the quantity of the various antiseptics should not be permitted to rise in food. But the difficulty of exact determination is very great, and, besides, this course would involve the concession of the whole principle, that a dealer in food has no right to add anything whatever to any article of food without due notice, and new antiseptics would be continually introduced, as they have been elsewhere, to circumvent any such partial restrictions. We might further, as another alternative, require that due notice be given by the vendor at the time of the sale that a preservative has been added to the article sold. Here, again, we know from experience how easy it is to circumvent such notice, and how ignorant the public are, and incapable to comprehend the notice. What use, for instance, would it be to inform a servant girl, at the time of sale, that a certain article contains a little boracic acid, or other substance, added from benevolent motives?

Our duty seems plain; we should work for entire prohibition of all kinds of preservatives. It is time that we went back to natural food. I object to be physicked indiscriminately by persons not qualified to administer medicine whilst I am in health; I object still more when I am ill. I object still more strongly to have my children physicked in their milk, or their bread and butter. It is no consolation to me to know that the physic is not immediately fatal, or not even violently injurious.

The practice is utterly unjustifiable except from the point of view of a dealer, who wants to make an extra profit, who wants to palm off a stale or ill-prepared article upon the public.

We owe our very existence, as public analysts, to the desire of the public to have a guarantee of the absolute purity of their food supply, and we would only be doing our duty if we did suppress the large and growing use of these objectionable chemicals called food preservatives.

## ON THE ADULTERATION OF FOOD WITH BORACIC ACID.

BY CHARLES E. CASSAL.

*Read at Meeting, November, 1890.*

THE increasing use of boracic acid, as well as of other so-called antiseptic agents for the preservation of articles of food, is a matter which demands immediate and most serious attention from public analysts. Inasmuch as my friend Mr. Hehner, with whom I have had several conversations on the subject, has consented to give the Society the benefit of his wide experience in this matter, I have thought that it would be convenient for the remarks which I should have to make upon it to be placed before the members in the form of a short paper at the same time. I propose, on this occasion at any rate, to deal with boracic acid only, because I have given some amount of attention to its use, and because I believe I was the first public analyst to officially certify milk and cream which contained it, as adulterated within the meaning of the Act. My first certificate was issued in 1887 upon a sample of cream which contained boracic acid; the local authority did not deem it advisable to take action at that time, and referred the matter to the Medical Officer of Health and to me, with the request that we should draw up a joint report to advise them whether the addition of boracic acid to milk and cream was injurious to health. This report was duly drawn up and presented. The matter excited some attention at the time, but, for reasons which I need not enter into here, no prosecution for adulteration with boracic acid was then undertaken.

Boracic acid is generally added to milk and cream in the form of certain proprietary articles, which are sold to the trade under different fancy names. Some of the more commonly used preparations, which consist of a mixture of boric acid (partly anhydrous and partly hydrated) with borate of soda, are added (in solution) in the proportion of *at least* 7 grains of the solid substance to the pint of milk. In cream it is generally added in *at least* double this quantity per pint. Inasmuch as both the farmer in the country and the dairyman in London are likely to use these preparations, these amounts may be largely increased. The amounts mentioned are also very likely to be exceeded through the carelessness or ignorance of those making use of such substances for preserving purposes.

But scanty information is to be obtained as to the action of boracic acid and borates on the human subject.

These substances do not appear to have been much used as internal remedies, and, accordingly, but little information as to their action is to be found in the text-books. One authority states that borax acts as a mild alkali on the alimentary canal; tending to render the fluids alkaline, and to cause diuresis; that it checks fermentation due to organisms, and is used as a diuretic and antacid. Another eminent authority who was consulted in connection with the report previously alluded to, refers to the tendency of these substances to set up diarrhœa, a disease very prevalent in hot weather, when the preservatives are most used to prevent the change which milk and cream are apt to undergo rapidly at a high atmospheric temperature. The medicinal dose of the acid as laid down in the British Pharmacopœia for an adult ranges from 5 to 30 grains, and, on the authority of my colleague, Dr. Dudfield, and of others, it may be computed that one-twelfth of the quantity, say a maximum of  $2\frac{1}{2}$  grains would be a suitable dose for a child under one year. It is quite possible that a strong, healthy infant, taking a quart of



milk daily might absorb as much as 20 or 25 grains in that time, having regard to the likelihood of the minimum amounts mentioned being exceeded.

The experiments of Dr. J. Förster, published some years since in a German scientific journal,\* go to show that the addition of boracic acid to articles of food in far smaller proportions than is customary is injurious to health. This author considers that "even small doses of it are injurious to the digestive organs." The injurious action, he says, depends on the circumstance that the drug acts so as to materially increase the proportion of solid matters and nitrogen in the faeces separated. Its action on the intestinal discharge is well marked, even by the exhibition of as little as 4 grains per diem, and is stated to be in direct relation to the quantity taken, and to be maintained for some time after the doses of the drug have ceased. The action described is perceptible, not only with vegetable or animal foods, which contain a large proportion of indigestible ingredients, but also when highly-digestible foods, such as milk and eggs, are taken. Food to which the acid has been added tends to cause an increase in the secretion of gall during assimilation. One of its most important actions, however, according to this author, is the increase which it causes in the discharge of albuminous substances from the intestinal canal.

E. Hötter has recently published a series of experiments on the action of boron compounds on plants. The absorption of such compounds was found by him to destroy the chlorophyll, and hence to arrest the processes of assimilation. The roots are affected, and soon die. Free boric acid was found to be more prejudicial than the alkali salts.

Apart from the experiments referred to, it is sufficiently plain that an "antiseptic" substance of any kind, if introduced into food must, by its very nature, be injurious to the health of the consumer. It is evident that the introduction of antiseptics of any kind into the alimentary canal must upset the conditions necessary to health. The danger is the greater because it is insidious, and because the effects produced are not violent or sudden, but such as will create disturbances and ultimately serious injury, which are likely to be ascribed to anything but the real cause. I consider that the question of quantity does not bear upon the matter in any way. I hope to show that it has, or should have, no bearing legally. Any quantity that is sufficient to produce the "antiseptic" effect in the food itself, must be regarded as injurious, even if the undoubtedly harmful action of continued small doses of a "preservative" substance be left out of consideration. It must be remembered that boracic acid preservatives are very extensively used. In butter, milk, cream, fish, meat, and in preserved foods and proprietary preparations of various kinds, boracic acid is to be constantly found. I have recently found it to be present in large amounts in meat "extracts" and "fluids" intended especially for the use of invalids and children, and which, I regret to say, are belauded in inflated language by members of the medical profession, who, *had they known* of the presence of boracic acid, would surely have condemned them. The unavowed presence of boracic acid in such preparations, or in the milk and cream so largely used by invalids and children might, and, as pointed out by a writer in the *British Medical Journal*, in most cases probably would seriously disturb a physician's course of treatment.

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\* Dingler.

Attempts have been made to confine the issue by asserting that it is as permissible to add boracic acid to a food as it is to add salt in certain instances (as in the case of salt meat). This contention is at once disposed of by pointing out the physiological fact that salt is a *food*, and that boracic acid is not. Again, boracic acid, and compounds of it, are not natural constituents of milk or of any food. They are not themselves "foods," but "drugs."

Proceedings could be taken against the vendors of milk containing boracic acid compounds under the 3rd Section of the Sale of Food and Drugs Act, which prohibits, with certain unfortunate reservations, the "mixing, colouring, staining, or powdering" of any article of food with any ingredient or material *so as to render* the article injurious to health. It is a matter of great difficulty, however, to prove "injury to health" to the satisfaction of an ordinary court. It is almost necessary in all such cases to be able to produce some poor creature who has been almost "done to death" by that which is complained of. Under this section also it is practically a necessity to state the percentage of the injurious substance; to afford, of course, a useful bone of contention for members of the legal profession, and not to obstruct in any way the wide loop-hole for the escape of offenders, duly left by the legislature, in this section. I contend that it is unnecessary to state percentage in a matter of this kind. The 6th Section of the Act makes it an offence to sell to the prejudice of the purchaser any article of food which is not of the "nature, substance and quality" of the article demanded by the purchaser, and provides that no offence is committed under this section if "any matter or ingredient not injurious to health" has been added, because such addition is required for the production or preparation of the food as "an article of commerce," or "in a state fit for carriage or consumption," and "not to conceal the inferior quality thereof." The 2nd Section of the Amendment Act of 1879 provides that it is no defence to prove that the "article of food in question, though defective in 'nature,' or in 'substance,' or in 'quality,' was not defective 'in all three respects.'" That is, proceedings would be justified by a defect in any one respect.

There appears, however, to be an impression abroad that there is no offence under the 6th section unless the adulterant forms "a substantial portion"—that is, presumably, more than a fractional part of the article as sold to the purchaser. Taking the case of milk, it ought hardly to be necessary to point out: (1) That milk containing boracic acid compounds is not of the nature, substance and quality of *milk*; (2) That even if defect in *nature* and *substance* is only constituted by the presence of an adulterant in what is popularly called "a substantial amount" (that is, forming a large integral portion of the article), defect in *quality* is at once established by the presence of boracic acid in milk, and that such defect is independent of the question of quantity; further (3) the admixture of boracic acid compounds with milk is not *required* for preserving it in course of transit from producer to consumer. Refrigeration, which adds nothing to the milk, is the recognised and legitimate method, if such preservation for transit be deemed necessary; and (4) the addition of the preservatives does serve the purpose of concealing the *inferior quality* of the milk, as it allows stale milk to be supplied as fresh, and as it is far more easy and less expensive than the better method of refrigeration.

I therefore hold that vendors of foods containing boracic acid compounds commit

offences under the 3rd and the 6th Sections of the Act of 1875, and the 2nd Section of the Amendment Act of 1879. Whether offences under the Act, however, are committed or not, I do not see how it is possible to arrive at any other conclusion but that the use of these preservatives is a serious form of adulteration. In my view, the absolute prohibition of their use is the only safe and proper course to take; although if it be desired to throw a sop to that large class of persons who are always morbidly anxious to follow middle courses, it may be admitted that the compulsory labelling of such "preserved" articles with the name of the substance or substances used, would be productive of great and immediate benefit. It is remarkable that those who defend the use of "preservatives," and assert them all to be "harmless," in any amount, should take such pains to conceal the fact that they have been used. In regard to several proprietary articles I have examined; I have had before me, apparently, the full details of the manufacture, given with the most child-like candour; everything, *except* the admixture of boracic acid, which was found in them all. In the case of certain "preserved" creams, it is asserted on the labels that "the cream being separated as soon as it is drawn from the cow, it will keep sweet longer." Comment upon this is needless.

Abroad, the use of "preservatives" is almost universally prohibited. If the legislature and if local authorities were in earnest about the suppression of adulteration, their use would be prohibited here. In any case, it is our duty as public analysts to fully advise those who appoint us about what is being done. The *onus* for not taking action will then not rest with us.

### DETECTION AND ESTIMATION OF BORACIC ACID IN MILK AND CREAM.

BY CHARLES E. CASSAL.

(*Read at Meeting, November, 1890.*)

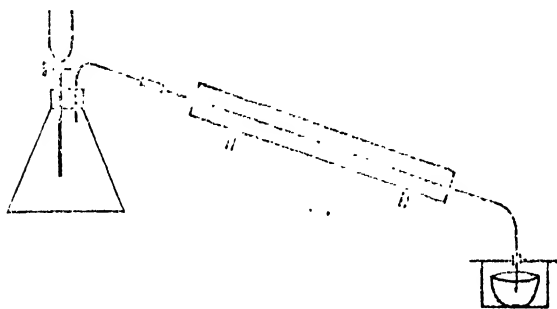
THE presence of boracic acid and borates in milk and cream can be detected without difficulty by applying the turmeric test and the alcohol-flame test to the ash.

The ash obtained in the course of the ordinary analysis is treated with a little water and made just acid with hydrochloric acid. Numbered slips of turmeric paper are moistened half way with the solution, and are preferably arranged on a glass plate and dried in the air bath; or a few drops of turmeric solution are added to the acidified ash, and evaporated to dryness in a porcelain capsule, the latter method being an exceedingly delicate one. On moistening with an alkali, the dark blue colour is obtained on the paper or porcelain when boracic acid is present. A dark blue solution is obtained when water and an alkali are added to the residue in the porcelain capsule, but the colour disappears with great rapidity, and I have hitherto been unsuccessful in determining the conditions which would render it permanent, or sufficiently permanent to admit of its being applied for purposes of estimation. The only method which up to the present I have found to be applicable for the estimation of boracic acid in milk and cream is a modification of that described by F. A. Gooch, in the *American Chemical Journal*, and which depends on the fact that free boracic acid can be completely separated from fixed substances by repeated distillation with methyl alcohol. I have repeated Mr. Gooch's experiments, and am able to confirm his results generally. He

states that methyl alcohol, ethyl alcohol and water are effective for the purpose of separation in the order named, and this I have found to be the case; but the volatilisation of even 0.2 grams. of anhydrous boric acid by the use of ethyl alcohol is so tedious that it is not advisable to use this substance for the purpose. Complete volatilisation of boric acid by the use of successive charges of methyl alcohol is easily and rapidly effected. I have found it best to use successive charges of 5 c.c. rather than 10 c.c., or more, as used by Mr. Gooch. I am not able to confirm his statement that in the presence of water methyl alcohol is not equally effective. My own experiments show that crystallised boracic acid is volatilised more rapidly than anhydrous boric acid, and that the addition of a few drops of water to the latter before evaporation or distillation with methyl alcohol promotes rather than retards the volatilisation of the acid.

The method as now applied by me for the estimation of the acid in milk and cream is as follows:—In the case of cream about 50 grams., and in that of milk about 100 grams. of the sample are rendered alkaline with caustic soda, evaporated to dryness and incinerated. The ash, which need not, of course, be burnt white, is ground up and transferred, washing in with a little methyl alcohol and a few drops of water, to a conical flask of from 200 c.c. to 300 c.c. capacity, provided with a doubly-perforated caoutchouc cork, through which pass a stop-cock funnel tube and a delivery tube. The flask is attached to an ordinary condenser by means of a flexible joint in such a way as to admit of its being shaken round occasionally, and is placed in an oil-bath. The mixture in the flask is acidified with acetic acid, and 5 c.c. of methyl alcohol is run in from the funnel tube, and distilled. The distillate is received in a weighed amount of pure lime (ignited to constant weight). About 1 gram. is a convenient quantity. The lime is contained in a platinum dish capable of holding about 70 c.c., which is placed in a glass receiver.

This receiver may be made from a ground-edged glass vessel, covered with a perforated ground-glass plate. The end of the condenser tube passes through a grooved or loosely-fitting cork in the perforation of the plate, and terminates just above the lime in the platinum dish.



Distillation with 5 c.c. of methyl alcohol is repeated several times, ten such treatments being ample for all likely cases. Fewer are generally quite sufficient. A gelatinous mixture is obtained in the platinum dish. It is well stirred, and allowed to stand for some minutes. It is then evaporated in an oil bath, and is finally heated over the blow-pipe

flame to constant weight. The increase of weight is boric acid, and the error does not in any case amount to more than 1 milligramme *plus* when dealing with from 0.1 to 0.25, or 0.3 grams. of anhydrous boric acid. To make sure that the acid has been completely volatilised, the residues in the distillation flasks are tested with turmeric paper.

The few drops of water added before the first distillation greatly increases the

rapidity of the removal of the boric acid. The use of nitric acid is not advisable for the purpose of freeing the boric acid in the flask. Acetic acid presents no difficulties, and is quite effective.

There is no advantage to be gained, in my opinion, from the use of the special apparatus described by Mr. Gooch in his paper, and the difficulties and inaccuracies attendant upon transference of the lime from crucible to flask, and from flask to crucible, are got over by carrying out the whole operation in one platinum dish.

My thanks are due to my assistant, Mr. Gerrans, for the care and trouble he has taken in helping me to carry out the necessary experiments.

#### DISCUSSION.

Mr. DAVIES said it appeared to him that the two papers they had just listened to opened up a large field for the consideration of public analysts, and personally he felt very much indebted to the two gentlemen who had brought them forward, particularly for the information that had been given with regard to the physiological effect of the boracic acid and borates, and for the general resumé of the whole field of information upon the subject. The fact was new to him that so many other states and countries had legislated on that particular subject, and that fact in itself was a very important reason in favour of there being legislation upon the matter here. He, personally, was disposed entirely to agree with the authors in the conclusions they arrived at that such additions of preservative agents are to be regarded as adulteration. That was the view he himself had held. He had asserted the presence of boracic acid in one or two cases, and although he had never actually certified to his vestry that it was an adulteration that called for their action, yet at the same time, when he had been asked in his capacity of analyst by private individuals, who had sent him samples, if he would regard such addition as adulteration, he had distinctly stated that such was his opinion, and that if such samples came before him in his capacity of public analyst they might expect that he would certify them to be adulterated in consequence of that addition. The papers would be exceedingly useful if they served to elicit the opinions of such public analysts as were present with regard to the question.

Mr. BLOUNT said that salicylic acid had been shown to be of different properties, according as it was natural or artificial, and possibly the injurious physiological action that had been noted was due to the fact that experiments had been conducted with the impure artificial variety.

Mr. ALLEN said that he fully agreed with what had fallen from Mr. Hehner as to its being the duty of public analysts to insist that articles of food should be what they represented to be. On the other hand he was not fully satisfied that some of these preservatives were so objectionable as the Governments of certain countries would seem to think; but he distinctly objected to the use of boracic in milk, as its addition was a direct encouragement to the milkmen to separate a portion of the cream and sell the partially skimmed milk the next day as new milk. Hence the detection of boracic acid in milk would strengthen the hands of the analysts who had occasion to report on a milk as deficient in cream or butter-fat. In fact, it was a fair inference from the presence of boracic acid that the milk was not new milk. With regard to the use of salicylic acid as a preservative, the difference in physiological effects of the natural and artificial acid might be safely ignored as in the small amounts of salicylic acid used it would be immaterial whether the salicylic acid was perfectly pure, or whether it contained a small admixture of cresotic acid such as often occurred in the commercial artificial acid. The use of salicylic acid for preserving beer seemed a less serious matter than its addition to milk. Fortunately

salicylic acid could be detected and separated with perfect certainty from matters containing it, and the same was true of benzoic acid. As to boracic acid, he congratulated Mr. Cassal on bringing before them so ready a method of estimating it. The method, though not strictly original, was little known to the majority of analysts.

Mr. Allen said he sympathised with any analyst who acted the part of pioneer. With regard to what had been said as to consultation with brother analysts before taking any decided action, he might remind them that the Society had not met for a period of five months, which was an undesirably long time. He thought the paper and comments on it showed the great value the Society had for its members.

Mr. ADAMS said that no better illustration could be given of the value of their meetings than that afforded by the papers just read by Messrs. Hehner and Cassal, and the remarks of the members present that had thereby been elicited; in all cases where a question arose such as these papers brought forward, it was a good thing that the views of the profession as a body could be ascertained, in order that some unanimity of action might follow, and mutual support and confidence fostered when circumstances necessitated new lines of action in reference to the official duties of the public analyst.

His own opinion with reference to the point at issue was that Mr. Cassal had used rather too strong a term when he said "*poisonous*"; but although boracic acid may not be poisonous in a general sense it did not follow that it may not sometimes be injurious—its effect probably might vary, and depend very much upon the individuals operated upon. It was well known that some drugs which act favourably on most people, seriously disagree with others, and even in ordinary matters of food it was astonishing what a variety of opinions were held by various people regarding the wholesomeness and digestibility of various food substances. He himself knew of a remarkable case of a gentleman who always suffered in a surprising manner after eating mutton—this food which is commonly regarded as being particularly easy of digestion, acted upon him as a violent poison—causing him to vomit, and to be purged; at first it was set down to some mistake or fancy on his part, but no, let the mutton be disguised in any way by mixture with other things, or by the addition of condiments, the same result always followed its ingestion, so that one might contend that it was impossible to predicate with certainty that any particular food or drug would be equally acceptable to all persons. In the speaker's opinion, therefore, in every case of preserved food it should be stated that such and such a food was preserved by the addition of salicylic acid or what not, so that the consumer might know what he was about to use. Moreover, he did not think any substance should be admitted into general use until its innocence had been established, until then it should be looked upon as an injurious, if not poisonous substance, and he thought this seemed to be the general opinion of the members of the society present.

Dr. VEITH said that he was very strongly of opinion that, so far as the London trade was concerned, there was no reason why fresh milk and cream should contain boracic acid, the best proof being that large quantities were sold daily to which no preservative had been added. But if someone went to any grocer's, poulterer's, cheesemonger's, or other shop, asking for potted cream which was expected to keep sweet for several days, and if that cream was found to contain boracic acid, he—Dr. Veith—must maintain that such cream certainly was of the nature, substance, and quality of the article demanded.

Mr. CASSAL said that the case which had been alluded to by Mr. Hehner was one in which he had certified a milk as having had at least 30 per cent. of the original fat abstracted, and as containing boracic acid. The authority had, therefore, not prosecuted on that point alone, but it was a part of the complaint as stated in their sum-

mons. The case was heard at petty sessions, and he was informed that the Chairman of the bench of magistrates in convicting the defendant severely reprimanded him, and made some strong remarks about the boracic acid adulteration. He certainly considered it most desirable that the public analysts of the country should fully discuss all matters of this kind, and that they should be as far as possible agreed. Squabbles between professional men in a law court were most injurious and discreditable. Public analysts did not act sufficiently in concert, and this was still one of the great evils of the profession, although matters were now much better than they used to be in this respect. But it was not always possible to consult one's colleagues, or to get a particular subject adequately discussed and a definite decision arrived at. It was plainly the public analyst's duty to certify milk containing boracic acid as adulterated. He could not act otherwise. The public authority who received the certificate might or might not take action upon it. This was no part of the analyst's business. If they took action he could not stand in the way of their doing so. He hoped that the Society would arrive at some decision in the matter.

Mr. HEINER said that he had not the remotest intention to express any censure upon Mr. Cassal for having taken action against a vendor of preserved food; on the contrary, he was thoroughly in accord with Mr. Cassal's opinion. But after public analysts had allowed, and almost encouraged, the use of food preservatives for many years—their open sale was no secret—it was rather hard now to suddenly turn round and to say to the dealers, "you have added a poisonous or injurious ingredient to the food you sold." As in the case which he mentioned in the beginning of his paper, there was abstraction of cream, the magistrate naturally did hold that this was aggravated by the addition of preservatives. He thought it would be desirable to select, as a test case, one in which no ordinary adulteration had been practised, such as the addition of boric acid to cream, or to otherwise genuine milk.

In his opinion, the injuriousness and otherwise of antiseptics was altogether beside the question. Granted that in at least 99 per cent. of food preservatives did no harm, the addition being unnecessary, was illegal under the Sale of Food Act. It should not be forgotten that in the process of digestion, bacterial organisms, especially in the lower portions of the intestines, played an important part in helping to break up such food matters as had escaped solution by gastric and pancreatic ferments. Food preservatives were added with the avowed object to prevent the growth of bacterial organisms, but we had a perfect right to object against the destruction of our intestinal bacteria, which, in all probability, were necessary aids to our nutrition, by our milkmen, buttermen, butchers and brewers.

Dr. Adams had alluded to the fact that certain persons might be affected by some preservatives, whilst others were not. In our ordinary feeding we all know this to be the case. If a person, for instance, from his experience knew that pork disagreed with him, he naturally would avoid eating it. But if a person was more or less affected by boric acid or other preservatives, how could he avoid it, as it was presented to him in so many articles of food without any notice whatever?

*(Conclusion of the Society's Proceedings.)*

## A METHOD FOR THE ESTIMATION OF ALBUMEN IN URINE.

By T. C. VAN NUYS AND R. E. LYONS.\*

THAT albuminous bodies are completely precipitated from solution by tannic acid is proven by the investigations of Liborius,† Girgensohn‡, Sebelien§, and others. By

\* "American Chemical Journal."

† Beitrag zu quant. Eiweissbestimmungen. Dorpat, 1871.

‡ Beiträge zur Albuminometrie. Dorpat, 1872.

§ Studien über die analyt. Bestimmungsweise der Eiweisskörper mit besonderer Rücksicht auf die Milch.

Sebelien's method of estimating the total quantity of albuminous bodies in milk, 3 to 5 grams. milk is diluted with some water, a few drops of a solution of sodium chloride or magnesium sulphate added, and the fluid is then treated with an excess of Almén's solution of tannic acid,\* the precipitate filtered off, well washed, and the nitrogen in the precipitate estimated by Kjeldahl's method.

The weight of nitrogen is multiplied by 6.37, the product of which is the weight of albuminous bodies in the weight of the milk taken. The factor 6.37 is the number of times the per cent. (15.7) of the nitrogen in albumen is contained in 100  $\left(\frac{100}{15.7} = 6.37\right)$ .

Sebelien's method differs from the methods of Almén and Liborius in not depending on the fixed constitution of the compound of albumen and tannic acid, but rather all of the albumen is separated from solution, and that all nitrogen compounds not albuminous can be removed from the precipitate by washing.

Our studies of this subject were carried on with the view of ascertaining if a method of estimating albuminous bodies in urine, employing tannic acid, is practical. As urine contains nitrogenous compounds in considerable quantities, the tannic acid compound of albumen is not easily washed until pure; besides, by continued contact of an acid, or acid salts, uric acid is precipitated, which would remain in part with the albumen; and as the volumetric method of estimating albumen with tannic acid has not been found accurate†, if there remains a practical method for estimating albumen in urine with tannic acid, it is that the total quantity of nitrogen in albuminous urine is first estimated, following which estimation is made of the quantity of nitrogen in the urine having its albumen separated by means of tannic acid. The difference in the quantities of nitrogen found is the weight of nitrogen of the albumen, which multiplied by 6.37, would give the weight of albumen. To determine if the method here outlined yields accurate results, the question arises if uric acid or other nitrogenous compounds of normal urine are retained by the precipitate formed by the tannic acid and albumen when filtered, so that the volume of urine in the undiluted filtrate would contain a smaller quantity of the normal nitrogenous constituents of the urine than is in a corresponding volume of urine before the separation of albumen.

To determine this we estimated the nitrogen in normal urine before and after the introduction and removal of known quantities of albumen. We determined if Almén's solution of tannic acid produces a separation of any part of the nitrogenous compounds of normal urine, or of urine containing an abnormal quantity of the urates, and finally we employed the new method and the gravimetric method in estimating the albumen in urine and compared the results.

Pure albumen was prepared by dissolving the whites of eggs in a small quantity of water, saturating the solution with magnesium sulphate and filtering. The filtrate was then treated with dilute acetic acid until a precipitate ceased to form, filtered off, and the precipitate washed with a saturated solution of magnesium sulphate.

\* 4 grams. tannic acid, 8 c.c. acetic acid (1 part glacial acetic acid and 3 parts water), 190 c.c. dilute alcohol, 50 per cent.

† Beiträge zur Albuminometrie von Girgensohn; Dorpat, 1872. Einige Methode zur Werthsbestimmungen der Milch von Tarazewicz; Dorpat, 1873.



Having pressed the precipitate between porous paper, it was dissolved in a small quantity of water, the solution neutralised with sodium hydrate, and dialysed until nearly all of the magnesium sulphate was separated. To the turbid solution of albumen a small quantity of the oil of thyme was added to prevent bacterial decomposition, and having mixed well, the solution was filtered. In case a solution was too dilute it was concentrated by evaporation at  $40^{\circ}$  to  $50^{\circ}$  C., and when nearly free of ash, some sodium chloride was added to facilitate the precipitation with tannic acid. Solutions of ovalbumen we number 1, 2, 3, etc.

#### FIRST ALBUMEN SOLUTION.

##### *Estimation of Albumen.*

- (1). 10 c.c. albumen solution, 10 c.c. water mixed.
  - (a). 5 c.c. of the solution required by Kjeldahl's method 47.3 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the solution required by Kjeldahl's method 47.3 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 0.1512 gram. nitrogen in 100 c.c. of the undiluted solution of albumen.
- (2). 10 c.c. albumen solution, 10 c.c. Almén's solution of tannic acid mixed and filtered without dilution.
  - (a). 5 c.c. of the filtrate required by Kjeldahl's method 49.9 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the filtrate required by Kjeldahl's method 49.95 c.c.  $\frac{1}{5}$  normal KOH, average 49.925 c.c., corresponding to 0.0084 gram. nitrogen of bodies not albuminous in 100 c.c. of the albumen solution. The quantity of nitrogen of bodies not albuminous deducted from the total quantity of nitrogen, 0.1512 gram. leaves 0.1428 gram. nitrogen of albumen, corresponding to 0.90963 gram. albumen in 100 c.c.

##### *Urine.*

- (1). 10 c.c. normal filtered urine, 10 c.c. water mixed.
  - (a). 5 c.c. of the diluted urine required by Kjeldahl's method 3.58 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the diluted urine required by Kjeldahl's method 35.8 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 1.5904 gram. nitrogen in 100 c.c. of the undiluted urine.
- (2). 20 c.c. urine, 10 c.c. albumen solution, 10 c.c. Almén's solution of tannic acid, mixed well in a small flask, and filtered without diluting.
  - (a). 5 c.c. of the filtrate required by Kjeldahl's method 35.75 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the filtrate required by Kjeldahl's method 35.8 c.c.  $\frac{1}{5}$  normal KOH, average 35.77 c.c., corresponding to 1.5932 gram. nitrogen in 100 c.c. of the undiluted urine; but as there was 0.0084 gram. nitrogen in 100 c.c. of the albumen solution which was not of the albumen, and therefore not precipitated by tannic acid, and the volume of No. 2, 5 c.c. is  $\frac{1}{4}$  albumen solution, there is  $\frac{1}{4}$  of 0.0084, 0.0021 gram. nitrogen bodies not albuminous of the urine, and consequently  $1.5932 - 0.0021 = 1.5911$  gram. nitrogen in 100 c.c. urine. Therefore there was a gain of 0.0007 gram. nitrogen by the process,  $1.5911 - 1.5904 = 0.0007$ .

#### SECOND ALBUMEN SOLUTION.

##### *Estimation of Albumen.*

- (1). 10 c.c. albumen solution, 10 c.c. water.
  - (a). 5 c.c. of the diluted solution required 47.9 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted solution required 48.0 c.c.  $\frac{1}{10}$  normal KOH, average 47.95 c.c., corresponding to 0.2296 gram. nitrogen in 100 c.c. of the undiluted albumen solution.

(2). 10 c.c. albumen solution, 5 c.c. Almén's solution, 5 c.c. water, mixed well in a small flask and filtered.

(a). 5 c.c. of the undiluted filtrate required 49.95 c.c.  $\frac{1}{10}$  normal KOH.

(b). 5 c.c. of the undiluted filtrate required 49.95 c.c.  $\frac{1}{10}$  normal KOH, corresponding to 0.0056 gram. nitrogen of bodies not albuminous in 100 c.c. of the undiluted albumen solution. Deducting the latter weight from the weight of the total quantity of nitrogen (0.2296 — 0.0056 = 0.224), there is 0.224 gram. nitrogen of the albumen in 100 c.c. of the solution, which corresponds to 1.42688 gram. albumen in 100 c.c. ( $0.224 \times 6.37 = 1.42688$ ).

#### *Urine I.*

(1) 10 c.c. normal filtered urine, 10 c.c. water.

(a). 5 c.c. of the diluted urine required 37.3 c.c.  $\frac{1}{10}$  normal KOH.

(b). 5 c.c. of the diluted urine required 37.35 c.c.  $\frac{1}{10}$  normal KOH, average 37.325 c.c., corresponding to 1.4196 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 10 c.c. urino, 5 c.c. Almén's solution, 5 c.c. water, mixed well in a small flask and filtered.

(a). 5 c.c. of the filtrate required 37.25 c.c.  $\frac{1}{10}$  normal KOH.

(b). 5 c.c. of the filtrate required 37.3 c.c.  $\frac{1}{10}$  normal KOH, average 37.275 c.c., corresponding to 1.4252 gram. nitrogen in 100 c.c. undiluted urine.

Deducting  $\frac{1}{4}$  of 0.0056 gram., the weight of nitrogen of bodies not albuminous, there remains 1.4238 gram. nitrogen in 100 c.c. of the undiluted urine. The results show a gain of 0.0042 gram. nitrogen in 100 c.c. of the undiluted urine after the separation of the albumen,  $1.4238 - 1.4196 = 0.0042$ .

*(To be continued.)*

### REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

ON COCO-NUTS. L. VAN ITALLIE. (*Ned. Tydschr. v. Pharmacie*). October, 1890.—A large nut contained about 155 grammes. of milky fluid of 1.022 specific gravity (at 18° C.) The reaction was faintly acid, and no precipitate was obtained on boiling or on addition of acetic or picric acids, showing the practical absence of albumenoids, which might have been expected in a so-called milk. 100 c.c. of the fluid were evaporated to a syrupy consistence and extracted with alcohol. The precipitate was washed on the filter with alcohol, but it readily dissolved in a little water. Delicate tests showed no traces of albumen, but the liquid readily reduced Fehling's solution. The filtrate was evaporated to a very small bulk, once more treated with alcohol, and the precipitate finally dissolved in water. The solution was not precipitated by picric acid, Mayer's solution, phospho-tungstic acid, potassium-cadmium iodide, platinic chloride, auric chloride, and tannic acid. Neither lead acetate nor the basic salt gave any precipitate, and no alkaloidal or glucosidal body was extracted by agitation with ether, chloroform, or benzol. 280 grammes of the endocarp were grated and pressed out. The fluid was precipitated with lead acetate, and the filtrate treated with liquor plumbi. The

precipitate was washed, suspended in alcohol, and decomposed with hydrogen sulphide. The filtrate from the lead sulphide was nearly colourless, and gave after evaporation no precipitate with the various general reagents for alkaloids. After boiling with dilute sulphuric acid, it did not reduce Fehling's solution, showing the absence of glucosides. The filtrate was freed from lead by a current of hydrogen sulphide, and evaporated to a syrupy consistence after neutralising the liberated acid. The liquid was mixed with alcohol, filtered, the alcohol evaporated, and the residue dissolved in water. The various reagents for alkaloids failed to produce any precipitate. Fehling's solution was reduced, but after removing the suboxide of copper, and boiling with dilute sulphuric acid, no further power of reducing copper solution was noticed, showing to the author's satisfaction the complete absence of any *alkaloids* or *glucosides* in the coco-nuts. To ascertain the nature of the sugars in the nuts, the author mixed 50 grammes. of the juice with a very slight excess of ammoniacal \* liquor plumbi. The filtrate showed undoubtedly the presence of sucrose by the usual tests. The lead precipitate was after washing suspended in water and treated with carbonic anhydride. The filtrate strongly reduced the Fehling, showing the presence of dextrose. The residue, which now might have contained the lead compound of levulose, was decomposed by hydrogen sulphide; but as the filtrate, after evaporation and neutralisation, did not reduce Fehling's solution, the absence of that substance may be taken for granted.

L. DE K.

ADULTERATION OF STARCH. F. DICKMANN. (*Zeitschr. f. Angew. Chemie.*) 1 Oct., 1890.—The author, in testing a sample of starch for ash by incinerating it in a platinum crucible, found his dish completely perforated, and to contain a lump of a metal. This consisted of lead, which was present in the sample as sulphate, to the extent of 17.6 per cent. Other mineral matter could not be detected. The moisture of the sample amounted to 11.75 per cent., and under the microscope the starch seemed to be all rice. The sample was not in powder but in the usual lumps, so there could be no question of an accidental contamination. The author is at a loss to understand what might have been the object of introducing a rather expensive article, such as lead sulphate, which has not even the power of improving the colour of the article.

L. DE K.

DETECTION OF MARGARINE IN BUTTER. BOCHAIRY. (*Ph. Zeit.*, 518).—Fifteen c.c. of the filtered butter-fat are put into a graduated cylinder, dissolved in 15 c.c. of toluene and 50 c.c. of commercial absolute alcohol are added. If the temperature does not exceed 18° C., the spirit will float on the top of the solution of the butter. The liquid must now be heated up to 50° C., and then thoroughly shaken. If the sample consists chiefly of margarine, the liquid gets at once turbid; but when one has to deal with a mixture, there forms no sensible deposit until the cylinder is put into water of 40° C. temperature. If the butter is adulterated, a more or less heavy layer will separate out. For instance, with a sample containing only 10 per cent. of margarine, 11 c.c. of deposit were obtained, but, unfortunately, the amount does not increase proportionately with the amount of margarine present. However, as a qualitative test, the process certainly deserves a fair trial.

L. DE K.

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\* Liquor plumbi mixed with ammonia until a permanent precipitate threatens to form.

ASSAY OF COMMERCIAL CAUSTIC SODA. G. LUNGE. (*Zeitschr. f. Angew. Chemie*, October, 1890).—As is well known, commercial caustic soda contains some soda compounds capable of saturating acids, which are consequently reckoned as sodium oxide. These compounds are sodium carbonate, silicate, or aluminate. In accurate commercial analysis the amount of sodium carbonate is generally calculated from the amount of carbonic anhydride the sample contains; but there seems to be a kind of unwritten agreement not to pay attention to the fact that some of the caustic soda found really exists as a silicate or an aluminate. This is most likely, because in practice (soap making, etc.), the presence of these compounds does not interfere with the manufacturing; and they are also generally present in but trifling quantities. The author's process of titrating with methyl-orange has been criticised by Cross and Bevan, who hold that the process is wrong because some of the alumina will also count as soda. The author points out that these chemists made a mistake in supposing two molecules of alumina to neutralise five molecules of sulphuric acid instead of six; and also that their idea about the interference of alumina is much exaggerated. The author has rarely found the amount of alumina to exceed .1 per cent., which is not astonishing, as the high temperature to which caustic soda is exposed during the fusion makes it deposit nearly all its impurities. Of course, the so-called caustic bottoms may contain sometimes as much as two per cent. of alumina, and cannot very well be titrated with the aid of methyl-orange.

---

L. DE K.

QUANTITATIVE ESTIMATION OF FLUORINE. H. OFFERMANN. (*Zeitschr. f. Angew. Chemie*, No. 20, 1890).—The author's process does not much differ from the one described in *THE ANALYST*, 1886, by Dr. S. Bein; but instead of weighing the separated silicic acid, the fluid is titrated with normal alkali, with tincture of cochineal as indicator. As 6 molecules of potassic hydrate = 1 molecule of hydrofluosilicic acid, 1 c.c. of normal alkali = .019 gramme of fluorine. The process gives good results even in presence of organic matter or volatile acids such as hydrochloric acid, and the author hopes that owing to its simplicity, the process will attract attention; but we fear that notwithstanding the excellent test analysis, few practical analysts will try it on account of the very complicated apparatus required.

---

L. DE K.

ESTIMATION OF FREE LIME IN THE BLACK SODA ASH. G. LUNGE. (*Zeitschr. f. Angew. Chemie*, October 1st, 1890).—This estimation is of some importance, as the presence of some free lime is indispensable to the complete extraction of the soda. The author gives his modification of Winkler's process, which, he thinks, will be found useful in the assay of black ash. Fifty grams. of the well-mixed sample are quickly powdered in a mortar, put into a 500 c.c. flask, and mixed with warm water, which must be free from carbonic acid. It is necessary to frequently shake the flask, otherwise a hard cake will form at the bottom. After two hours the liquid is made up to the mark, and after thorough shaking 5 c.c. of the turbid liquid are pipetted off, put into a beaker, and mixed with a slight excess of barium chloride. After adding a few drops of phenol-phthalein, the alkalinity (lime) is now titrated with  $\frac{1}{10}$ -oxalic acid. The author found it totally unnecessary to add sugar, a plan proposed to better dissolve the lime.

---

L. DE K.

ASSAY OF LOGWOOD. DR. L. SCHREINER. (*Chem. Zeit.*, No. 58, 1890).—The author did not intend to publish his process, which he has for years successfully employed; but as many correspondents believe, the accurate assay of logwood is still an impossibility, he

has finally decided to make his process known. Fifty grams. of the ground wood are completely exhausted with water, the liquid diluted up to 1 litre, and a portion of it filtered through hide powder, which must be of sound and woolly quality. The filtrate is generally colourless, and even remains so after addition of ammonia. 100 c.c. of this solution, and also 100 c.c. of the original solution, are evaporated to dryness at 100° C, and the difference between the two weighings represents the amount of colouring matters, including, of course, tannin. For the assay of extract of logwood, 10 c.c. of the powdered sample are dissolved in water and diluted up to 1 litre. To see if there is any adulteration with mineral matter, the ash is taken as well. L. DE K.

**TESTING FOR ARSENIC BY FELEITMANN'S METHOD.**—Professor Johnson has recently shown the great advantage of employing aluminium instead of zinc in this test, because commercial aluminium never contains arsenic, while it is very difficult to obtain zinc that is absolutely free from this impurity. The evolution of hydrogen from aluminium and potassium hydrate also proceeds with great regularity and without the application of heat to any extent.

**DETECTION OF WOOD-PULP IN PAPER.** WURSTER, MAANDBL VERVALSCH, No. 189.—By means of the following reagents, which must be applied in the presence of an acid, either in the cold or at a gentle heat, the presence of wood-pulp in paper may be readily detected.

| Reagent.       | Wood-paper.      | Cellulose. |
|----------------|------------------|------------|
| Orcine.        | Dark red.        | No colour. |
| Resorcine.     | Dark green.      | Violet.    |
| Pyrogallol.    | Greenish blue.   | "          |
| Phenol.        | Greenish yellow. | "          |
| Phloroglucine. | Blueish violet.  | No colour. |

Another excellent reagent is dimethyl-paraphenylene-diamine, which colours the wood intensely fuchsia red, and enables the analyst to approximately estimate its quantity.

**POPULAR CHEMISTRY.**—The following specimen of chemistry for the million has appeared in the *Echo*, and we reproduce it for the delectation of our readers:—Sixty samples of milk, a dozen samples of flour, bread, meat extracts, potted meats, feeding cakes, etc., can be estimated with the greatest facility, as regards flesh-forming constituents, in an hour. The cost is almost *nil*. One grain of permanganate of potash in solution made acid constitutes sixty workable measures, or *subnormes*. With a slight alteration of the process, alcohol, starch, mucilage can be estimated in the same rapid manner. The cost is so insignificant that a million may be made for a guinea. The only apparatus required are a pipette and flask, and a phial and bottle may be substituted even for these. The calculation required is quite within the capacity of a Board School lad of the sixth standard. The process has lately been brought under the notice of the Agricultural Department and School Board authorities, and will speedily make an impression on vestries, as it has already done in the grain trade. Details may be found in various agricultural papers of the month notably the *North British Agriculturist* of the 22nd and 29th ult., and subsequently. The whole of the experiments may be performed by every householder, and the pipette and flask will take their place the same as scales and weights amongst household requisites. Never has the individual possessed such power over the value of his food stuffs. A kernel of wheat, a few grains of bread, a few drops of milk, such is the test of vegetable and animal albumens.

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# THE ANALYST.

JANUARY, 1891.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL MEETING of the Society was held at Burlington House on Wednesday, the 10th ult., the President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

The following gentlemen were elected as members:—

Mr. J. J. Beringer, F.I.C., F.C.S., Public Analyst for Cornwall; Dr. J. B. Readman, Analytical Chemist, Edinburgh.

As Associate, Mr. J. F. H. Gilbard, assistant to Mr. Dyer.

The following were proposed for election as members:—

Mr. F. H. Perry Coste, Analytical Chemist, London; Mr. Leo Taylor, Analytical Chemist, Walthamstow.

As Associate, Mr. H. W. Wood, assistant to Mr. Clayton.

The following paper was read:—

“On the Composition of Butter.” By Dr. Veith.

The Annual Meeting will be held at Burlington House on Wednesday, the 14th inst.

The Annual Dinner will afterwards be held. Full particulars will be duly announced.

## ON THE COMPOSITION OF BUTTER.

By DR. P. VIETH.

*Read at Meeting, December, 1890.*

WHEN speaking about the analysis of butter, we are, at the present time, very much inclined to think exclusively of ascertaining whether the chief component part of butter, *i.e.* the fat, consists of the pure fat derived from cow's milk. No doubt, the admixture of foreign fat to butter is a widely practised and very serious offence, and the detection of such adulteration, with a view to put a stop to it, is a matter of the greatest importance. But over this prominent question we must not forget that there are other ways in which the purchaser and consumer of butter may be wronged. The remarks which I have to offer have some reference to the latter, and do not touch the former question of adulteration with foreign fats. My observations, moreover, are not addressed to the public analyst in particular, but to the analytical chemist in general.

We all are well aware of the difficulties to fix standards or limits of purity for natural products, such, for instance, as milk ; but these difficulties also exist with regard to manufactured articles, those derived from milk, notably, cream— if the term “ manufactured article ” is allowed to be used—and butter, forming striking examples.

When milk or cream is subjected to continuous dashing, the fat globules coalesce in consequence, it is assumed, of the fat constituting the globules, passing from the liquid into the solid state. After churning has gone on for a time, conglomerates of fat make their appearance and grow larger by continued dashing. The fatty mass thus obtained and removed from the liquid in which it floats—the buttermilk—is raw butter. In order to make of the raw product the article of trade it is necessary to remove part of the buttermilk enclosed in the raw butter, which is done by kneading the latter. The further treatment which butter receives differs with the habits of the various producing countries and the tastes of the consumers for which the finished product is intended. Thus, while in some countries kneading alone is resorted to as a means for the removal of the excess of buttermilk, in others this removal is done more effectually by washing the butter with water or brine. Again, certain kinds of butter, more particularly those made from sweet cream and intended for immediate consumption, contain no salt, or very trifling quantities of it, while others, those made from sour milk or cream and meant to be kept for some time without exception, have salt added, frequently in considerable quantities.

Salt is added to butter, not only to meet the taste of certain classes of consumers, but also as a preserving agent. Judging from the experience of others, as well as from my own, I am inclined to believe that the habit of adding other preservatives, notably those containing boracic acid, to butter is becoming very general in certain places.

One more extraneous matter frequently, perhaps one might say invariably, present in butter of commerce is some colouring agent. No doubt the colouring of butter originally arose out of a desire to give to all butter, which under certain circumstances is nearly as white as tallow, that rich yellow colour which fresh grass-butter is known to present, a kind which has the renown of being of especially delicate flavour. Nowadays, however, no one, when putting colouring to the milk or cream before churning, thinks of making appear like grass-butter the white-looking product of the milk of his stall-fed cows. The reason why butter is coloured is simply this: the trade demands an article which from one end of the year to the other should be as uniform as possible in every respect, and uniformity of colour is one of the first qualities expected. Butter-colouring is made exclusively of cake annatto, a harmless and clean preparation of the fruit of *Bixa orellana*, which has nothing to do with the nasty soft annatto preparation of by-gone times. The quantity of colouring used being extremely small, and its nature perfectly innocuous, there can scarcely be any reason to object to a practice which is nothing but a concession to the trade. The great importance which the butter trade has attained may be gathered from the fact that last year's import of butter into this country amounted to 1,927,469 cwt., worth £10,243,728, whilst the export was not quite 25,000 cwt. I am not aware of the existence of any statistics which would allow to state what the home-production amounts to ; it must, however, be very considerable.

I have mentioned that butter is frequently washed, in order to free it as much as

possible from buttermilk; the complete removal of the latter, if intended, is certainly not achieved in practice. The kneading of the butter also does not rid it of all the buttermilk, or the water used for washing out the latter, as the case may be, and, indeed, a product consisting entirely of butter-fat and containing no water would not be butter at all. On the other hand, the presence of an undue amount of butter-milk or water is not only highly undesirable, but may even be looked at as a fraud.

The question then arises in what proportion the various constituents should be present, and in the absence of any other guidance, I believe this question of standards and limits with regard to butter can only be satisfactorily decided by referring to the usual composition of butter as it appears in the market. The 267 analyses of butter samples which I have made in the course of the last few years might, perhaps, form a contribution to the solution of the question.

The way in which I proceed in analysing butter is described in a few words:—Into a conical flask of about four ounces capacity 4 or 5 grams. of butter are introduced. The flask is put in a drying oven, the temperature of which is kept at 100° C., and the evaporation of the water facilitated by giving the melted butter a circular motion every half-hour. After the loss in weight has been ascertained, the fat is completely washed out with ether, and the insoluble part dried and weighed. In a watery extract of the non-fatty solids the chlorine is titrated. We have then determined water, fat, solids-not-fat and sodium chloride contained in the latter and calculated from the chlorine. The difference between the quantities of solids-not-fat and sodium chloride is made up by the small amount of the non-fatty solids of milk retained by the butter, and may, for convenience sake, here be termed “curd, etc.” In case the butter should contain extraneous admixtures other than salt—for instance preservatives, so far as they are not soluble in ether—these would, of course, swell the last-named item.

Turning now to the results of my analyses, I do not propose to harrass you with all the figures relating to the 267 samples forming the basis of my observations, but will confine myself to giving maxima, minima, and averages for the various kinds of butters:—

| Description of Butter.     | Number of Samples. | Fat.                 | Water.               | Curd, etc.        | Salt.             |
|----------------------------|--------------------|----------------------|----------------------|-------------------|-------------------|
| English, fresh and salt .. | 72                 | 82.97—90.49<br>86.85 | 7.85—14.39<br>11.54  | .02—1.55<br>.59   | .00—2.44<br>1.02  |
| French, fresh              | 108                | 82.83—86.61<br>84.77 | 11.63—15.57<br>13.76 | .46—2.17<br>1.38  | .00—.51<br>.09    |
| French, salt ..            | 5                  | 82.30—86.25<br>84.34 | 11.15—13.59<br>12.05 | 1.26—1.85<br>1.60 | 1.30—2.54<br>2.01 |
| Kiel, salt ..              | 40                 | 82.00—89.45<br>85.24 | 8.39—15.23<br>12.24  | .80—2.82<br>1.17  | .73—2.06<br>1.35  |
| Danish, salt ..            | 17                 | 78.05—87.57<br>83.41 | 9.58—17.25<br>13.42  | .94—2.39<br>1.30  | 1.06—3.05<br>1.87 |
| Swedish, salt ..           | 25                 | 78.91—85.64<br>82.89 | 11.78—16.96<br>13.75 | .77—2.01<br>1.33  | 1.12—3.00<br>2.03 |



## THE ANALYST.

With regard to the fat, I may say at once that I am of opinion that in a well-made butter it should not fall below 80 per cent. Among my samples there were three only in which the percentage of fat was below 80, viz., one sample of Danish butter with 78·05, and two samples of Swedish butter with 79·69 and 78·91 per cent. respectively. The extreme in the other direction was shown by a sample of English butter which contained 90·49 per cent. of fat.

We have next to consider the quantity of water. An undue percentage of this should be objected to, if not for others, certainly for this reason, that it reduces below its proper limit the percentage of fat, which latter after all is what we chiefly want to buy in butter. On the other hand the reduction of the water below a certain limit can be effected only by "over-working" the butter, a process which very injuriously affects the appearance and taste, and thereby the commercial value of the product. Moreover, in the case of salt butter a certain amount of water is required to dissolve the salt which has been incorporated into the butter, and keep it in solution.

The results of my examinations were as follows:—

| Percentage of Water. | Number of Samples. | Per cent. |
|----------------------|--------------------|-----------|
| 7— 8                 | 1                  | ·4        |
| 8— 9                 | 6                  | 2·2       |
| 9—10                 | 6                  | 2·2       |
| 10—11                | 16                 | 6·0       |
| 11—12                | 39                 | 14·6      |
| 12—13                | 46                 | 17·2      |
| 13—14                | 103                | 38·6      |
| 14—15                | 38                 | 14·2      |
| 15—16                | 10                 | 3·8       |
| 16—17                | 1                  | ·4        |
| 17—18                | 1                  | ·4        |
|                      | 267                | 100·0     |

From this statement it appears that the percentage of water generally varies from 11 to 15, and that it rarely rises above 16, nor falls below 10. The samples of French butter are remarkable for their great uniformity in composition, which is explained by the fact that in Normandy large packing establishments exist which are supplied with freshly churned butter from a number of dairies, and make this butter up for the London market by blending and working it. In the samples of English-made butter the water was worked out more completely than in the remaining samples.

Speaking now on the item which I have termed "curd, etc.," I will exclude the samples of French butter, because some of them at least contained boracic acid. No preservative was found in samples of the other kinds of butter. The quantity of "curd etc.," is of particular interest if considered in conjunction with the quantity of water present, as such consideration enables us to make some inferences as to the way in which the butter had been manufactured.

Milk contains for every 100 parts of water about 10 parts of solids free of fat. The same relation between the two items must exist in buttermilk and also in butter, provided the latter was made from sweet or slightly sour milk or cream and freed from the excess of buttermilk by kneading. If the butter, as is the fashion in some countries, is rinsed with water when taken from the churn, the relation referred to will be somewhat effected, and, still more it will be disturbed if the butter is thoroughly washed with water or brine. The influences mentioned will, I need hardly say, reduce the relative quantity of "curd, etc." On the other hand, the relative quantity will be increased if butter is made from strongly acid material in which the casein had been not coagulated in soft, but precipitated in hard masses, which partially become enclosed in and are retained by the butter.

For every 100 parts of water, there were present,

| PARTS OF "CURD, ETC.," |      |    |      |       |           |
|------------------------|------|----|------|-------|-----------|
| In English butter,     | min. | 0, | max. | 13,   | average 5 |
| „ Kiel                 | „    | „  | 8,   | „ 23, | „ 10      |
| „ Danish               | „    | „  | 7,   | „ 14, | „ 10      |
| „ Swedish              | „    | „  | 7,   | „ 16, | „ 10      |

We may consider, then, the Kiel, Danish, and Swedish butters not, or very slightly washed—rinsed—and the English butters, in the majority of cases, very thoroughly washed. As an instance of a butter made of strongly acid material, I may mention a sample of Kiel butter in which the relation between water and "curd, etc." was 100 to 23; this butter had a decidedly "cheesy" taste.

The quantity of salt was very small in all the samples of fresh French butter, there being generally less than .1 per cent. present, proving that no salt had been incorporated into the butter. The same was the case with a number of the samples of English butter, others of the same class containing a few tenths of a per cent. of salt, pointing to washing with brine. Far the majority of samples of salt butter contained from 1 to 2 per cent. salt, a small number between 2 and 3 per cent., and one sample of Danish butter just above 3 per cent. I may mention that when salt is added to raw butter, about half its quantity only is retained by the butter, while the other half is lost in the buttermilk which is worked out.

In conclusion, I will apologise for having entered rather much into practical details which may perhaps be considered as in no way concerning the members of this Society. My excuse is, that I am of opinion that some knowledge of practical details is very frequently highly desirable for the chemical expert.

#### DISCUSSION.

Mr. ALLEN said they were greatly indebted to Dr. Vieth for the valuable statistics he had laid before them. Hitherto the most extensive published series of determinations of salt and water in butter were those contained in the report of the Board of Inland Revenue, dated May 31st, 1876, describing the results of the analysis of 117 samples of butter collected in various parts of the kingdom. In these samples Dr. James Bell found proportions of water ranging from 4.15 to 20.75 per cent., the mean of the whole being 14.20 per cent. One of the above so-called "genuine" samples contained 15.08 per cent. of salt, the next highest quantities being 9.20, 8.56, 8.38, 8.28, and 7.71 per cent. In one sample there was 4.02 per cent. of curd in addition to 19.12 per cent. of water. In the same report Dr. Bell stated that "the samples may be taken as fairly

representing the various qualities of butter as made and brought to market by farmers both in England and Ireland. Every care was exercised by the Board's local officers in procuring them, and there can be no question whatever as to their being *genuine*." From this conclusion it is evident that in Dr. Bell's opinion no farmer purposely leaves excess of water in his butter, and if any dairy-maid, through laziness or incompetency, produce a butter containing an excessive proportion of water, the percentage of water thereafter allowable in butter is to be increased accordingly. This line of argument would be laughable if, as a matter of fact, it had not had the lamentable effect of raising the legal allowable proportion of water to 21 per cent. He (Mr. Allen) had met with a still larger proportion of water in butter sent for analysis under the Sale of Food Act, and conviction had occurred on his certificate for 23 per cent. He should regard 16 per cent. as the maximum proportion of water in good, well-made butter. Any excess above this proportion became evident in the course of the analysis, and it was only in such cases that it became necessary to ascertain the amount exactly. Dr. Vieth had pointed out that a good deal of the salt added to butter was eliminated in the subsequent treatment. In the North of England the public gave preference to butter containing considerably more salt than met the London taste.

Mr. CASSAL said that an important question had been raised with regard to the definitions of composition which should be applied to articles of food, such as butter. It led him to suggest that the Council should consider whether it would not be advisable for the Society to lay down such definitions as were required. It was easy to see the difficulty in which public analysts were placed, in the present state of the law, by such circumstances as the one which had been mentioned—that a dairymaid in Ireland should manufacture an abnormal butter, and thereby endeavour to create an exception to the definitions which had been adopted by public analysts. If the Somerset House chemists based their limits upon the results of analysis of abnormal samples of this kind, it would be greatly to the detriment of the public and of the public analyst; but he did not think that this was the case. The best definition which the promoters of the Margarine Act were apparently able to hit upon was, that "'butter' was to be the article usually known as 'butter.'" As a matter of fact, public analysts were acting upon definitions which they had themselves made, and which were based upon such work as that of Dr. Vieth, whose results were, as all would admit, of the greatest value and importance. It would be highly satisfactory if, at the instance of the Society, both public analysts and private analysts throughout the country could be induced to adopt, uniformly and fairly, wide and sensible definitions as might commend themselves for acceptance after careful consideration.

Mr. HEHNER wished to remind Mr. Cassal that the Society of Public Analysts, within a year or two of the commencement of its existence, laid down a limit that butter should contain not less than 80 per cent. of butter fat, a figure that had been fully confirmed by subsequent results.

Mr. ADAMS said that Dr. Vieth had given them some useful statistics, and, coming from him, they were all the more valuable to himself not being a public analyst, and therefore looking at the matter from a broad, commercial, and perfectly independent point of view. The speaker's own view of the case was that it was quite as much the duty of the public analyst to keep the watering of butter within just limits as that of the reduction of spirits, whiskey, gin, etc., by unfair dilution.

Mr. FABER said there had been cases in police courts where dealers had been convicted of selling butter containing an undue amount of water.

Dr. VIETH, in reply, said that with regard to limits being fixed for butter, he quite agreed that this was desirable, and, as he had said, he put his figures before them in

the hope they might be of some use in this respect. At the same time he must say that this was one of those points upon which they should feel their way very carefully. While of opinion that 80 per. cent. ought to be the lowest limit for fat, he would not think it right that a butter containing 80 per. cent. of fat should contain 20 per. cent. of water, the water in this case would certainly be in excess. Two only of his samples contained above 16 per. cent., and that he thought ought to be the highest limit. Mr. Allen had mentioned that he did not think it necessary to determine the quantity of water in every case, because the sample showed it at once, but that was very deceptive. Some butters look as if they contained no water at all, and still there was a very appreciable quantity present. There might be as much as 25 per. cent. of water present in a butter, and it was not at all certain that the butter would have a suspicious appearance.

*(Conclusion of the Society's Proceedings.)*

## A METHOD FOR THE ESTIMATION OF ALBUMEN IN URINE.

By T. C. VAN NUYS AND R. E. LYONS.

*(Concluded.)*

### *Urine II.*

(1). 10 c.c. normal filtered urine, 10 c.c. water.

(a). 5 c.c. of the diluted urine required 35.0 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 34.95 c.c.  $\frac{1}{5}$  normal KOH, average 34.975 c.c., corresponding to 1.6828 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 10 c.c. filtered urine, 5 c.c. albumen solution, 5 c.c. Almén's solution mixed well in a small flask and filtered.

(a). 5 c.c. of the filtrate required 34.9 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 35.0 c.c.  $\frac{1}{5}$  normal KOH, average 34.95 c.c., corresponding to 1.6856 gram. nitrogen in 100 c.c. undiluted urine; and by deducting the weight of the nitrogen of bodies not albuminous in the solution, 0.0014, there remains 1.6842 gram. nitrogen in 100 c.c. of the undiluted urine. By the results obtained there was found 0.0014 gram. more nitrogen in 100 c.c. of the undiluted urine after the separation of the albumen than there was in the same volume of undiluted urine before the addition of albumen.

## THIRD ALBUMEN SOLUTION.

### *Estimation of Albumen.*

(1). 10 c.c. albumen solution, 10 c.c. water.

(a). 5 c.c. of the diluted solution required 44.4 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted solution required 44.35 c.c.  $\frac{1}{5}$  normal KOH, average 44.375 c.c., corresponding to 0.63 gram. nitrogen in 100 c.c. of the undiluted solution.

(2). 10 c.c. undiluted albumen solution, 10 c.c. Almén's solution, mixed well and filtered. The filtrate was free of nitrogen.

0.63 gram. nitrogen corresponds to 4.0131 grams. albumen in 100 c.c. of the solution.

### *Urine.*

(1). 10 c.c. filtered normal urine, 10 c.c. water.

(a). 5 c.c. of the diluted urine, 38.7 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine, 38.8 c.c.  $\frac{1}{5}$  normal KOH.

(c). 5 c.c. of the diluted urine, 38.75 c.c.  $\frac{1}{5}$  normal KOH, average 38.75 c.c., corresponding to 1.26 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 10 c.c. normal filtered urine, 5 c.c. albumen solution, 5 c.c. Almén's solution, mixed well and filtered.

(a). 5 c.c. of the filtrate required 38.8 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 38.8 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 1.2544 gram. nitrogen in 100 c.c. of the undiluted urine, or 0.0056 gram. nitrogen less than in 100 c.c. of the urine before the separation of albumen.

#### FOURTH ALBUMEN SOLUTION.

##### *Estimation of Albumen.*

(1). 10 c.c. albumen solution, 10 c.c. water.

(a). 5 c.c. of the solution required 48.9 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the solution required 49.0 c.c.  $\frac{1}{5}$  normal KOH, average 48.95 c.c. corresponding to 0.0588 gram. nitrogen in 100 c.c. of the undiluted solution.

(2). 10 c.c. albumen solution, 10 c.c. Almén's solution, mixed well and filtered.

The filtrate was free of nitrogen. 0.0588 gram. nitrogen corresponds to 0.3745 gram. albumen in 100 c.c. of the undiluted solution.

##### *Urine.*

(1). 5 c.c. normal filtered urine, 25 c.c. water.

(a). 5 c.c. of the diluted urine required 47.65 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 47.7 c.c.  $\frac{1}{5}$  normal KOH, average 47.675 c.c. corresponding to 0.7812 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 5 c.c. urine, 20 c.c. albumen solution, 5 c.c. Almén's solution, mixed and filtered.

(a). 5 c.c. of the filtrate required 47.7 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 47.7 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 0.7728 gram. nitrogen in 100 c.c. of the undiluted urine, therefore 0.0084 gram. of nitrogen less than in 100 c.c. of the urine before the separation of albumen.

#### FIFTH ALBUMEN SOLUTION.

##### *Estimation of Albumen.*

(1). 10 c.c. albumen solution, 10 c.c. water.

(a). 5 c.c. of the solution required 49.55 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the solution required 49.6 c.c.  $\frac{1}{5}$  normal KOH, average 49.57 c.c., corresponding to 0.04816 gram. nitrogen in 100 c.c. of the undiluted solution.

(2). 10 c.c. albumen solution, 5 c.c. Almén's solution, 5 c.c. water, mixed and filtered.

The filtrate was free of nitrogen. 0.04816 gram. nitrogen corresponds to 0.3067 gram. albumen in 100 c.c. of the undiluted solution.

##### *Urine.*

(1). 10 c.c. normal filtered urine, 10 c.c. water.

(a). 5 c.c. of the diluted urine required 32.5 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 32.45 c.c.  $\frac{1}{5}$  normal KOH, average 32.47 c.c., corresponding to 1.9633 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 15 c.c. urine, 9 c.c. albumen solution, 6 c.c. Almén's solution, mixed and filtered.

(a). 5 c.c. of the filtrate required 32.5 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 32.5 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 1.96

gram. nitrogen in 100 c.c. undiluted urine. Therefore there was found 0.0033 gram. nitrogen less in 100 c.c. of the urine after the addition and removal of the albumen,  $1.9633 - 1.96 = 0.0033$ .

## SIXTH ALBUMEN SOLUTION.

*Estimation of Albumen.*

(1). 10 c.c. albumen solution, 10 c.c. water.

(a). 5 c.c. of the diluted solution required 48.0 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted solution required 48.05 c.c.  $\frac{1}{5}$  normal KOH, average 48.025 c.c., corresponding to 0.2212 gram. nitrogen in 100 c.c. of the undiluted solution.

(2). 10 c.c. albumen solution, 10 c.c. Almén's solution, mixed and filtered. The filtrate was free of nitrogen.

0.2212 gram. nitrogen corresponds to 1.4090 gram. albumen in 100 c.c. of the solution,  $0.2212 \times 6.37 = 1.4090$ .

*Urine I.*

(1). 20 c.c. normal filtered urine, 20 c.c. water.

(a). 5 c.c. of the diluted urine required 38.1 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 38.05 c.c.  $\frac{1}{5}$  normal KOH, average 38.07 c.c., corresponding to 1.3361 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 20 c.c. urine, 10 c.c. albumen solution, 10 c.c. Almén's solution, mixed and filtered.

(a). 5 c.c. of the filtrate required 38.1 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 38.15 c.c.  $\frac{1}{5}$  normal KOH, average 38.125 c.c., corresponding to 1.33 gram. nitrogen in 100 c.c. of the undiluted urine. Therefore there was found 0.0061 gram. nitrogen less in 100 c.c. of the urine after the addition and removal of the albumen,  $1.3361 - 1.33 = 0.0061$ .

*Urine II.*

(1). 20 c.c. normal filtered urine, 20 c.c. water.

(a). 5 c.c. of the diluted urine required 40.45 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 40.4 c.c.  $\frac{1}{5}$  normal KOH, average 40.425 c.c., corresponding to 1.0724 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 20 c.c. urine, 10 c.c. albumen solution, 10 c.c. Almén's solution, mixed and filtered.

(a). 5 c.c. of the filtrate required 40.4 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 40.5 c.c.  $\frac{1}{5}$  normal KOH, average 40.45 c.c., corresponding to 1.0696 gram. nitrogen in 100 c.c. of the undiluted urine. Therefore there was found 0.0028 gram. nitrogen less in 100 c.c. of the undiluted urine after the addition and removal of the albumen,  $1.0724 - 1.0696 = 0.0028$ .

## SUMMARY OF RESULTS.

| Albumen Solution. | Grams. Albumen in 100 c.c. of the Solution. | Total grams. Nitrogen in 100 c.c. of the Urine. | Dilution of the Urine. | Variation in quantity of Nitrogen in grams, in 100 c.c. of the Undiluted Urine before introduction of Albumen and after its removal. |
|-------------------|---|---|------------------------|--|
|                   |   |   |                        |  |
| I                 | 0.9096                                      | 1 1.5904  | 1 to 2                 | +0.0007  |
| II                | 1.4268                                      | 1 1.4196  | 1 to 2                 | +0.0042  |
| II                | 1.4268                                      | 1 1.6828  | 1 to 2                 | +0.0014  |
| III               | 4.0131                                      | 1 1.2600  | 1 to 2                 | —0.0056  |
| IV                | 0.3745                                      | 0 0.7812  | 1 to 6                 | —0.0084  |
| V                 | 0.3607                                      | 1 1.9633  | 1 to 2                 | —0.0033  |
| VI                | 1.4090                                      | 1 1.3360  | 1 to 2                 | —0.0061  |
| VI                | 1.4090                                      | 1 1.0724  | 1 to 2                 | —0.0028  |

In case the urine is diluted to a greater degree than 1 to 2, the limit of error in the estimated quantity of nitrogen increases as the quantity of nitrogen decreases by the dilution.

This is understood from the fact that with 5 c.c. urine, 0.1 c.c. of the  $\frac{1}{5}$  normal KOH corresponds to 0.0056 gram. nitrogen in 100 c.c. of the urine; and if the urine be diluted from 1 to 2 or 1 to 4, 0.1 c.c.  $\frac{1}{5}$  normal KOH corresponds to 0.012 and 0.0224 gram. nitrogen respectively. To determine if uric acid or other nitrogenous compound in normal, acid, or neutral urine, separates by contact with tannic acid, as in Almén's solution, in different periods of time, the following estimations were made:—

#### NORMAL URINE I.

##### *Estimation of Nitrogen.*

- (1). 10 c.c. of filtered urine, 10 c.c. water.
  - (a). 5 c.c. of the diluted urine required 47.25 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the diluted urine required 47.3 c.c.  $\frac{1}{5}$  normal KOH, average 47.275 c.c., corresponding to 0.3052 gram. nitrogen in 100 c.c. of the undiluted urine.
- (2). 10 c.c. filtered urine, 10 c.c. Almén's solution, mixed well in a small flask, let stand 15 minutes and filtered.
  - (a). 5 c.c. of the filtrate required 47.3 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the filtrate required 47.25 c.c.  $\frac{1}{5}$  normal KOH, average 47.275 c.c., corresponding to 0.3052 gram. nitrogen in 100 c.c. of the undiluted urine.
- (3). 10 c.c. filtered urine, 10 c.c. Almén's solution, mixed well in a small flask, let stand 45 minutes and filtered.
  - (a). 5 c.c. of the filtrate required 47.2 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the filtrate required 47.2 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 0.3136 gram. nitrogen in 100 c.c. of the undiluted urine.
- (4). 10 c.c. filtered urine, 10 c.c. Almén's solution, mixed well in a flask, let stand 60 minutes and filtered.
  - (a). 5 c.c. of the filtrate required 47.25 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the filtrate required 47.3 c.c.  $\frac{1}{5}$  normal KOH, average 47.275 c.c., corresponding to 0.3052 gram. nitrogen in 100 c.c. of the undiluted urine.

From the results of these estimations it seems that no nitrogen compound was separated from the urine by contact with the tannic acid solution, even when the time was extended to one hour, but the urine in this case contained a minimum quantity of nitrogen, and it may be inferred that the urine contained a minimum quantity of uric acid.

#### NORMAL URINE II.

Urine was highly coloured, acid in reaction, sp. gr. 1.031

##### *Estimation of Nitrogen.*

- (1). 10 c.c. filtered urine, 10 c.c. water.
  - (a). 5 c.c. of the diluted urine required 31.95 c.c.  $\frac{1}{5}$  normal KOH.
  - (b). 5 c.c. of the diluted urine required 31.9 c.c.  $\frac{1}{5}$  normal KOH, average 31.925 c.c., corresponding to 2.0244 grams. nitrogen in 100 c.c. of the undiluted urine.
- (2). 10 c.c. urine, 10 c.c. Almén's solution, mixed well in a flask, let stand 20 minutes and filtered.

(a). 5 c.c. of the filtrate required 31.8 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 2.0384 grams. nitrogen in 100 c.c. of the undiluted urine.

(3). 10 c.c. urine, 10 c.c. Almén's solution, mixed well in a flask, let stand 45 minutes and filtered.

(a). 5 c.c. of the filtrate required 32.0 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 2.016 grams. nitrogen in 100 c.c. of the undiluted urine.

(4). 10 c.c. urine, 10 c.c. Almén's solution, mixed well in a flask, let stand 60 minutes and filtered.

(a). 5 c.c. of the filtrate required 32.1 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 32.1 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 2.0048 grams. nitrogen in 100 c.c. of the undiluted urine.

The increased quantity of nitrogen found in the urine after having stood with the tannic acid 20 minutes was due either to absorption of ammonia from the air of the laboratory or to an error in the titrations, probably from the latter, as but one estimation was made.

By contact with tannic acid 45 and 60 minutes, the losses of nitrogen were 0.0084 and 0.0196 gram. respectively. As 0.075 c.c. of the  $\frac{1}{5}$  normal KOH corresponds to 0.0084 gram. nitrogen when the dilution is 1 to 2, there is no evidence that any nitrogen compound, uric acid, was separated by the contact, but that there was a loss of nitrogen by the urine remaining in contact with tannic acid 60 minutes is probable.

In order to subject urine containing an abnormal quantity of uric acid, pure urate of potassium was dissolved in normal urine, neutral in reaction; solution having taken place, the urine was filtered and the uric acid in the filtrate estimated. The quantity of uric acid in 100 c.c. urine was 0.3575 gram., corresponding to about 6 grams. uric acid eliminated in 24 hours.

#### *Estimation of Nitrogen.*

(1). 10 c.c. of the filtered urine containing the potassium urate, 10 c.c. water.

(a). 5 c.c. of the diluted urine required 32.2 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 32.2 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 1.9801 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 10 c.c. filtered urine, 10 c.c. Almén's solution, mixed well in a small flask, let stand 20 minutes and filtered.

(a). 5 c.c. of the filtrate required 32.4 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 32.45 c.c.  $\frac{1}{5}$  normal KOH, average 32.425 c.c., corresponding to 1.9684 gram. nitrogen in 100 c.c. of the undiluted urine. The results of the estimations indicate the separation of 0.0117 gram. nitrogen in 100 c.c. of the urine by contact with the tannic acid.

Albumen was next estimated by this method, and also in the same urine by the gravimetric method.

#### ALBUMINOUS URINE I.

(1). 30 c.c. filtered urine, 10 c.c. water.

(a). 5 c.c. of the diluted urine required 40.3 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 40.35 c.c.  $\frac{1}{5}$  normal KOH.



(c). 5 c.c. of the diluted urine required 40.25 c.c.  $\frac{1}{5}$  normal KOH, average 40.3 c.c. corresponding to 0.72426 gram. nitrogen in 100 c.c. undiluted urine.

(2). 30 c.c. filtered urine, 10 c.c. Almén's solution, mixed well and filtered.

(a). 5 c.c. of the filtrate required 41.1 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 41.2 c.c.  $\frac{1}{5}$  normal KOH.

(c). 5 c.c. of the filtrate required 41.15 c.c.  $\frac{1}{5}$  normal KOH, average 41.15 c.c., corresponding to 0.6608 gram. nitrogen in 100 c.c. of the undiluted urine. The difference in the quantities of nitrogen estimated in 1 and 2 is 0.06346 gram., corresponding to 0.40424 gram. albumen in 100 c.c. urine.

*The Gravimetric Method.*

The average of three estimations of albumen in 100 c.c. of the urine was 0.4399 gram., hence the difference in the results of both methods is 0.0357 gram. albumen in 100 c.c.

ALBUMINOUS URINE II.

(1). 10 c.c. filtered urine, 10 c.c. water.

(a). 5 c.c. of the diluted urine required 40.9 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 40.9 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 1.0192 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 10 c.c. filtered urine, 10 c.c. Almén's solution, mixed well in a flask and filtered.

(a). 5 c.c. of the filtrate required 40.95 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 41.0 c.c.  $\frac{1}{5}$  normal KOH, average 40.97 c.c., corresponding to 1.01136 gram. nitrogen in 100 c.c. of the undiluted urine. The difference in the quantities of nitrogen in 100 c.c. of the urine before and after the separation of albumen is 0.00784 gram., corresponding to 0.04994 gram. albumen in 100 c.c. of urine.

*The Gravimetric Method.*

The average of two estimations of albumen in 100 c.c. of the urine was 0.0506 gram., hence the difference in the results of both methods is 0.0006 gram.

ALBUMINOUS URINE III.

(1). 30 c.c. of the filtrated urine, 20 c.c. water.

(a). 5 c.c. of the diluted urine required 34.35 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the diluted urine required 34.3 c.c.  $\frac{1}{5}$  normal KOH, average 34.32 c.c., corresponding to 1.4634 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 30 c.c. filtered urine, 20 c.c. Almén's solution, mixed and filtered.

(a). 5 c.c. of the filtrate required 35.7 c.c.  $\frac{1}{5}$  normal KOH.

(b). 5 c.c. of the filtrate required 35.8 c.c.  $\frac{1}{5}$  normal KOH, average 35.75 c.c., corresponding to 1.33 gram. nitrogen in 100 c.c. of the undiluted urine. The difference in the quantities of nitrogen in 100 c.c. before and after the separation of albumen is 0.1334 gram., corresponding to 0.8497 gram. albumen in 100 c.c. of the urine.

*The Gravimetric Method.*

The average of three estimations of albumen by the gravimetric method was 0.8557 gram. albumen in 100 c.c. of the urine, hence the difference in results obtained by both methods is 0.006 gram. albumen in 100 c.c. of the urine.

ALBUMINOUS URINE IV.

(1). 20 c.c. of the filtered urine, 10 c.c. water.

- (a). 5 c.c. of the diluted urine required 35.75 c.c.  $\frac{1}{5}$  normal KOH.  
 (b). 5 c.c. of the diluted urine required 35.85 c.c.  $\frac{1}{5}$  normal KOH, average 35.8 c.c., corresponding to 1.1928 gram. nitrogen in 100 c.c. of the undiluted urine.  
 (2). 20 c.c. filtered urine, 10 c.c. Almén's solution, mixed and filtered.  
 (a). 5 c.c. of the filtrate required 36.1 c.c.  $\frac{1}{5}$  normal KOH.  
 (b). 5 c.c. of the filtrate required 36.1 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 1.1676 gram. nitrogen in 100 c.c. of the undiluted urine. The difference in the quantities of nitrogen found before and after the removal of the albumen is 0.0252 gram., corresponding to 0.1605 gram. albumen in 100 c.c. of the urine.

*The Gravimetric Method.*

The average of two estimations of albumen by the gravimetric method was 0.1551 gram. albumen in 100 c.c. of the urine, hence the difference in results obtained by the two methods is 0.0054 gram. in 100 c.c. urine.

ALBUMINOUS URINE V.

- (1). 20 c.c. filtered urine, 10 c.c. water.  
 (a). 5 c.c. of the diluted urine required 36.00 c.c.  $\frac{1}{5}$  normal KOH.  
 (b). 5 c.c. of the diluted urine required 36.15 c.c.  $\frac{1}{5}$  normal KOH, average 36.1 c.c., corresponding to 1.1676 gram. nitrogen in 100 c.c. of the undiluted urine.  
 (2). 20 c.c. filtered urine, 3 c.c. of Almén's solution, 7 c.c. water, mixed and filtered.  
 (a). 5 c.c. of the filtrate required 38.2 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 0.9912 gram. nitrogen in 100 c.c. of the undiluted urine. The difference in the quantities of nitrogen found before and after the removal of the albumen is 0.1764 gram. corresponding to 1.1236 gram. albumen in 100 c.c. of the undiluted urine.

*The Gravimetric Method.*

The average of two estimations of albumen by the gravimetric method was 1.1292 gram. albumen in 100 c.c. of the urine; the difference, therefore, in the results obtained by the two methods is 0.0056 gram. albumen in 100 c.c. urine.

ALBUMINOUS URINE VI.

- (1). 20 c.c. filtered urine, 10 c.c. water.  
 (a). 5 c.c. of the diluted urine required 40.85 c.c.  $\frac{1}{5}$  normal KOH.  
 (b). 5 c.c. of the diluted urine required 40.75 c.c.  $\frac{1}{5}$  normal KOH, average 40.8 c.c., corresponding to 0.7728 gram. nitrogen in 100 c.c. of the undiluted urine.  
 (2). 20 c.c. filtered urine, 4 c.c. Almén's solution, 6 c.c. water, mixed and filtered.  
 (a). 5 c.c. of the filtrate required 42.9 c.c.  $\frac{1}{5}$  normal KOH.  
 (b). 5 c.c. of the filtrate required 42.9 c.c.  $\frac{1}{5}$  normal KOH, corresponding to 0.5964 gram. nitrogen in 100 c.c. of the undiluted urine; the difference, therefore, in the quantities of nitrogen found before and after the removal of the albumen is 0.1764 gram., corresponding to 1.1236 gram. albumen in 100 c.c. of the undiluted urine.

*The Gravimetric Method.*

The average of two estimations of albumen by the gravimetric method was 1.1279 gram. albumen in 100 c.c. of the urine; hence the difference in the result obtained by the two methods is 0.0043 gram. albumen in 100 c.c. of the urine.

ALBUMINOUS URINE VII.

- (1). 20 c.c. filtered urine, 10 c.c. water.

(a). 5 c.c. of the diluted urine required 40.4 c.c.  $\frac{1}{10}$  normal KOH, corresponding to 0.8064 gram. nitrogen in 100 c.c. of the undiluted urine.

(2). 20 c.c. filtered urine, 5 c.c. Almén's solution, 5 c.c. water, mixed and filtered.

(a). 5 c.c. of the filtrate required 41.5 c.c.  $\frac{1}{10}$  normal KOH, corresponding to 0.714 gram. nitrogen in 100 c.c. of the undiluted urine.

The difference in the quantities of nitrogen found before and after removal of the albumen is 0.0924 gram., corresponding to 0.5885 gram. albumen in 100 c.c. of the undiluted urine.

*The Gravimetric Method.*

The average of two estimations of albumen by the gravimetric method was 0.5953 gram. albumen in 100 c.c. of the urine. The difference in the results obtained by the two methods is 0.0068 gram. albumen in 100 c.c. of the urine.

SUMMARY OF RESULTS.

| Albuminous<br>Urine. | Per Cent. of Albumen<br>by New Method. | Per Cent. of Albumen<br>by Gravimetric Method. | Difference<br>in Results. |
|----------------------|--|--|---------------------------|
| I.                   | 0.4042                                 | 0.4399   | 0.0357                    |
| II.                  | 0.0499                                 | 0.0506   | 0.0006                    |
| III.                 | 0.8497                                 | 0.8557   | 0.006                     |
| IV.                  | 0.1605                                 | 0.1551   | 0.0054                    |
| V.                   | 1.1236                                 | 1.1292   | 0.0056                    |
| VI.                  | 1.1236                                 | 1.1279   | 0.0043                    |
| VII.                 | 0.5885                                 | 0.5953   | 0.0068                    |

By the results of estimations of albumen made by the two methods, the average error is 0.0092 per cent., the maximum being 0.0357 per cent., the minimum 0.0006 per cent.

The average error in 35 estimations of albumen made by Dillner,\* employing the method of Esbach and the gravimetric method, is 0.054 per cent., the quantity of albumen in the urine being from 0.05 to 2.13 per cent.

In 73 per cent. of a great number of estimations of albumen in urine made by O. Hammarsten,† employing Brandberg's method and the gravimetric method, the average error is nearly 0.05 per cent.; however, in many cases, the error reached 0.1 per cent.

In estimating albumen in urine by the new method a great excess of tannic acid should not be employed in separating the albumen, as it is oxidised very slowly by sulphuric acid. For ordinary quantities of albumen in urine equal volumes of Almén's solution and urine are sufficient, for small quantities one volume of Almén's solution and two volumes of urine, and in case the albumen is two per cent. the urine should be diluted with water from one to two volumes before making the estimations.

To separate the albumen, 10 c.c. of the filtered urine is introduced with 10 c.c. Almén's solution into a 50 c.c. flask, and after mixing well, the fluid is filtered through a dry filter-paper into a dry beaker. 5 c.c. of the filtrate is subjected to the action of 10 c.c. concentrated sulphuric acid, as in the original method of Kjeldahl. Whether the dilution of the urine is 1 to 2 or 1 to 3, the albuminous

\* Esbachs Albuminimeter. Upsala Läkareför. Förhand. 21, 1886.

† Upsala Läkareförenings Förhandlingar 18, 139.

urine is diluted to the same degree, and 5 c.c. is employed in Kjeldahl's method. To absorb the ammonia, 10 c.c. normal sulphuric acid is employed. In calculating the quantity of albumen in urine from the results of the estimations, instead of subtracting the weight of nitrogen of 100 c.c. of the urine proper from the weight of the total quantity of nitrogen in 100 c.c. containing albumen, and multiplying the difference by 6.37 for the quantity of albumen, the process may be shortened in the following way: Subtract the number of c.c.  $\frac{1}{2}$  normal KOH employed in the two titrations, and multiply the difference by 0.0028, and the product of which by 40. The final product is the quantity of nitrogen in 100 c.c. of the undiluted urine, which, multiplied 6.37, gives the per cent. of albumen. If the urine is diluted from 1 to 3 volumes in both cases, the weight of nitrogen is multiplied by 60, to obtain the quantity of nitrogen in 100 c.c. of the undiluted urine.

Serum-albumen and serum-globulin, the bodies estimated by the gravimetric method, are not exactly of the same chemical constitution, and hence the employment of the factor 6.37 would not lead to correct results in all cases. The per cent. of nitrogen in serum-globulin, according to Hammarsten, is 15.85, while the per cent. of nitrogen in serum-albumen is 15.7. The factor with which to multiply the weight of nitrogen to obtain the weight of serum-globulin is 6.31 instead of 6.37. As a rule, however, serum-globulin accompanies serum-albumen in the urine in small quantities, so that the number 6.37 may be employed with comparative safety. On the other hand, for exact pathological investigations, the weight of nitrogen of albuminous bodies excreted by the kidneys affords a more certain datum than the quantity of albumen. This is apparent when the fact is taken into consideration, that the per cent. of albumen in the urine, as determined by any of the methods now employed, does not represent a definite weight of nitrogen. The new method has the additional advantage of determining the total quantity of nitrogen of the normal nitrogenous constituents of the urine, which, taken into account with the weight of nitrogen of albuminous bodies, is doubtless of importance to the pathologist.—*Chemical Laboratory, Indiana University, Bloomington.*

## STUDY OF A METHOD FOR THE QUANTITATIVE DETERMINATION OF SUCROSE, INVERT-SUGAR AND DEXTROSE, OR LEVULOSE.

By F. G. WIECHMANN, PH.D.\*

### PART I.

THE quantitative determination of sucrose, invert-sugar and dextrose, or levulose, when these substances occur together, presents a problem of considerable interest and importance.

Winter† suggested a method of separating sucrose from dextrose and levulose, and dextrose from levulose. It consists in adding ammoniacal acetate of lead,‡ made immediately before use, to the solution of the sugars, until there is no further precipitation. The precipitate, which is ordinarily of a dazzling white colour, is digested with a great amount of water, and then filtered.

The filtrate contains the sucrose as a lead compound. Decompose this compound

\* School of Mines Quarterly.

† *Zeitschrift des Vereines für Rübenzucker-industrie*, 1888, vol. xxxviii., page 782.

‡ Add ammonia to acetate of lead as long as the precipitate just continues to disappear.

by carbonic acid gas, and filter off the carbonate of lead. This solution then contains the sucrose.

Wash the residue thoroughly with water, then suspend it in water and saturate with carbonic acid gas. This gives a filtrate and a residue. The filtrate contains the dextrose. The precipitate consists of carbonate of lead and of a compound of lead with levulose. Wash well with water, then suspend the precipitate in water and pass in sulphuretted hydrogen. The precipitated sulphide of lead is filtered out, washed thoroughly, and the filtrate, to which the washings have been added, is concentrated on a water-bath, and the levulose in it determined.

This method aims at the actual separation of the sucrose, the dextrose and the levulose, and thus, of course, permits of the separate determination of each constituent. But even if this method were perfectly satisfactory and reliable, which the writer, from his experiments, is strongly inclined to question, even then it would hardly prove a desirable method for an analytical determination on account of the time required for its execution.

Other attempts to determine levulose and dextrose when in combination, have been attempted. These are, however, based either entirely or partially on optical analyses.

As, however, fluctuations of temperature affect to a marked degree polariscopic determinations of invert-sugar solutions (invert-sugar, levulose), it seemed to the writer that a method which should be entirely independent of optical analyses, and be based wholly on data obtained by gravimetric methods, would be the most desirable.

Tollens, in his *Kurzes Handbuch der Kohlenhydrate*, 1888, contains the following :—

“If levulose is mixed with dextrose, or with any other glycoses less sensitive to acids, the sum of the glycoses may be determined with Fehling’s solution. Then the levulose may be destroyed by hydrochloric acid, according to Sieben’s directions, and, after neutralising by sodic hydrate, the remaining dextrose may be determined, and the difference calculated as levulose.”

If a reliable process could be based on this suggestion, it would prove a simple and rapid method for the estimation of the sugars named, when occurring together.

In the following pages there will be described a course of analyses, and the methods of calculation deemed necessary to attain the desired result.

The estimations to be made consist of the following :—

1. Total sucrose.
2. Total reducing sugars.
3. Dextrose, after destruction of the levulose by Sieben’s method.

For the tables expressing the relation between the copper precipitated and the sucrose, the invert-sugar, the dextrose and levulose respectively, reference must be made to the memoirs cited.

The Fehling solution, used in all of the following determinations, has consisted of :

Sulphate of copper, crystallised, 34·639 grammes in 500 c.c. of water.

Rochelle salts, crystallised, 173·000 grammes in 400 c.c. of water.

Sodic hydrate, crystallised, 50·000 grammes in 100 c.c. of water.

## I. DETERMINATION OF TOTAL SUCROSE.\*

Weigh out 13.024 grammes of sample. Dissolve with about 75 c.c. of water in a 100 c.c. flask.† Add 5 c.c. of hydrochloric acid containing 38 per cent. HCl (specific gravity, 1.188). Heat in two or three minutes on a water-bath up to between 67° and 70° C. Then keep at this temperature (as close to 69° C. as possible) for five minutes, with constant agitation. Cool quickly and make up to 100 c.c. Remove 50 c.c. by a pipette, place in a litre flask, and fill up to 1000 c.c. Of this solution take 25 c.c. (corresponding to 0.1628 gramme of sample), neutralise the free acid present by 25 c.c. of a solution of sodium carbonate, prepared by dissolving 1.7 grammes of crystallised sodium carbonate in 1000 c.c. of water. Then add 50 c.c. of Fehling's solution, heat to boiling as directed in determination of total reducing sugars, and boil for three minutes.

## II. TOTAL REDUCING SUGARS.‡

Weigh out 26.048 grammes. Place into a 100 c.c. flask, clarify with basic acetate of lead, make up to 100 c.c., filter and polarise. Take an aliquot part of the filtrate, add sodium sulphate to remove any lead present, make up to a definite volume, and filter. It is best to arrange the dilution so that the 50 c.c. of this filtrate, which are to be used for the determination of the total reducing sugar, will precipitate between 200 and 300 mgrs. of copper.

To 50 c.c. of the sugar solution prepared as above, add 50 c.c. Fehling's solution (25 c.c. copper sulphate and 25 c.c. of Rochelle salt-soda solution).

Over the wire gauze above the flame lay a sheet of asbestos, provided with a circular opening of about 6.5 cm. diameter; on this place the flask, and arrange the burner in such a manner that about four minutes are consumed in heating the solution to the boiling-point. From the time that the solution starts to boil—the moment when bubbles arise not only from the centre but also from the sides of the vessel—continue to boil for exactly two minutes, with a small flame. Then remove the flask from the flame immediately, and add 100 c.c. cold distilled water from which the air has previously been removed by boiling.§

Then filter through an asbestos filter, wash and reduce to metallic copper.

This operation is carried out in the following manner: Clean thoroughly a small straight calcium chloride tube, or any other tube of similar pattern. Introduce asbestos fibres || so as to fill about half of the bulb. Draw air through while drying, cool and weigh. Connect with aspirator, filter the precipitated  $\text{Cu}_2\text{O}$ , wash with hot water, then, having changed the receiving flask, wash twice with absolute alcohol and twice with ether. Having removed the greater part of the ether by an air-current, connect the upper part of the filter tube by means of a cork and some glass tubing with a hydrogen apparatus, and heat with a small flame, whose tip is about 5 cm. below the

\* German Government Method. See *Die Deutsche Zuckerindustrie*, 1888. *Besondere Beilage zu*, No. 27.

† Do not add any basic acetate of lead for clarifying purposes, as this will introduce a source of error, and yield results too low.

‡ *School of Mines Quarterly*, vol. ix, No. 1, 1888.

§ The water is added to prevent subsequent precipitation of cuprous oxide.

|| The asbestos must first be prepared by washing successively with a solution of caustic soda (not too concentrated), boiling water, nitric acid, and again with boiling water. When filled into the glass tube, the asbestos is made to rest on a perforated platinum cone.

bulb containing the  $\text{Cu}_2\text{O}$ . The reduction in the current of hydrogen gas is finished in two or three minutes.<sup>†</sup>

After the asbestos-tube has been cooled in the current of hydrogen, air is drawn through and the tube is then weighed.

After an analysis is completed, the asbestos is readily freed from the adhering copper by washing with dilute nitric acid.

### III. DEXTROSE BY ALLIHN'S METHOD.\*

Take 30 c.c. copper sulphate solution, 30 c.c. Rochelle salt-soda solution,<sup>†</sup> 60 c.c. water. Heat to boiling. Then add 25 c.c. of the solution to be tested, which must, however, not contain more than 1 per cent. of the active substance, and boil for two minutes. Then proceed as before, filtering, reducing the cuprous oxide, etc.

### IV. LEVULOSE BY LEHMANN'S METHOD.‡

Take 25 c.c. copper sulphate solution, 25 c.c. Rochelle salt-soda solution,<sup>§</sup> 50 c.c. water. Heat to boiling. Then add 25 c.c. levulose solution, which must not contain more than 1 per cent. of the active substance. Boil for fifteen minutes, and proceed as previously directed.

### SIEBEN'S METHOD FOR DESTRUCTION OF LEVULOSE.||

Take 100 c.c. of a solution made to contain 2.5 grammes of the dry substance (invert-sugar, or invert-sugar and levulose), place in a flask, add 60 c.c. six times normal strength  $\text{HCl}$ , and heat in a boiling water-bath for three hours. Cool immediately, neutralise with six times normal strength  $\text{NaOH}$  solution, make up to 250 c.c. and filter. Of the filtrate use 25 c.c. to determine dextrose according to Allihn.

The calculation of the results obtained by these methods here described is effected as follows :—

#### *Calculation.*

The calculation consists of two steps. Step 1 is always the same, and merely establishes whether the dextrose and the levulose are present in the proportion of 1 : 1, or, whether either is in excess. Step 2 determines the amount of this excess, be it of dextrose or of levulose.

The values analytically determined are :

No. 1 = Cu reduced by total sucrose + total reducing sugars.

No. 2 = Cu reduced by total reducing sugars.

No. 3 = Cu reduced by dextrose (after Sieben's treatment).

STEP I.—No. 1 is Cu reduced by inverted sucrose + total reducing sugars. No. 2 is Cu reduced by total reducing sugars.

No. 1 minus No. 2 is Cu reduced by inverted sucrose. Report the corresponding value as sucrose. The difference between No. 1 and No. 2, divided by 2, represents the Cu reduced by the dextrose of the inverted sucrose. Call this value  $x$ .

\* E. Wein, *Tabellen zur Quantitativen Bestimmung der Zuckerarten*, 1888.

† 173 grammes Rochelle salts and 125 grammes potassic hydrate are dissolved in water and made up to 500 c.c.

‡ E. Wein, *Tabellen zur Quantitativen Bestimmung der Zuckerarten*, 1888.

§ Prepared by dissolving 346 grammes Rochelle salts and 250 grammes sodic hydrate in water and making up to 1 litre.

|| *Zeitschrift des Vereines für Rübenzucker-industrie*, vol. xxxiv. p. 869.

No. 3 is Cu reduced by total dextrose (after Sieben's treatment).  $x$  is Cu reduced by the dextrose of the inverted sucrose.

No. 3 less  $x$  is Cu reduced by the dextrose of the total reducing sugars. Call this value  $y$ .

$y \times 2 = 2y$ . Cu reduced by invert-sugar + free dextrose, if any be present. Compare this value,  $2y$ , with No. 2.

If  $2y =$  No. 2 invert-sugar *only* is present. If so, report as invert-sugar.

If  $2y >$  No. 2 free dextrose is present.

If  $2y >$  No. 2 free levulose is present.

STEP II.—When  $2y >$  No. 2. Free dextrose is present.

No. 2 is Cu reduced by total reducing sugars.  $y =$  Cu reduced by the dextrose from the total reducing sugars.

No. 2 minus  $y =$  Cu reduced by the levulose of the total reducing sugars. Call this value  $p$ .

$p \times 2 = 2p =$  Cu reduced by invert-sugar. Report as invert-sugar.

No. 2 is Cu reduced by total reducing sugars.  $2p =$  Cu reduced by invert-sugar.

No. 2 minus  $2p =$  Cu reduced by free dextrose.

STEP II. When  $2y >$  No. 2. Free levulose is present.

No. 2 is Cu reduced by the total reducing sugars.  $2y =$  Cu reduced by invert-sugar. Report as invert-sugar.

No. 2 minus  $2y =$  Cu reduced by the free levulose.

In these calculations no attention has been paid to the fact that the reducing-power of invert-sugar, dextrose and levulose is not identical. The reducing-power of dextrose being considered as 100, that of invert-sugar is 96, and that of levulose is 94.\*

For very accurate work the necessary corrections for these variations must be made.

In order to test the applicability of the method here described for determining invert-sugar, dextrose and levulose, the following experiments were carried out:

Four series of experiments were made, embracing, respectively, mixtures of:

- I. Invert-sugar and dextrose.
- II. Invert-sugar and levulose.
- III. Sucrose, invert-sugar and dextrose.
- IV. Sucrose, invert-sugar and levulose.

Of course, from the very nature of the test, the sucrose becomes inverted, and so really Series III. and IV., as well as I. and II., are only mixtures of invert-sugar and dextrose, or of invert-sugar and levulose; but the proportions between the invert-sugar and the dextrose, or the levulose, respectively in Series III. and IV., have been so arranged as to approximately correspond to the composition of certain raw sugars.

(To be continued.)

#### NEW BOOKS.

CHEMICAL ARITHMETIC, PART I. A COLLECTION OF TABLES, MATHEMATICAL, CHEMICAL, AND PHYSICAL, FOR THE USE OF CHEMISTS AND OTHERS. BY W. DITTMAR, LL.D., F.R.S. GLASGOW: W. HODGE AND CO., 26 BOTHWELL STREET.

THIS work is intended to ultimately consist of two parts, the first of which contains all the tables and constants, while the second is to be an exposition of their application to the solution of all arithmetical problems connected with chemistry. The first volume is

\* Soxhlet, *Journal für Praktische Chemie*, vol. xxi., pp. 289 and 290.



now before us, and it may be at once admitted that Dr. Dittmar has produced an exceedingly useful and complete book, and that his claim to have provided the general analyst with a set of tables and constants sufficient for all his ordinary routine work, without going further, is entirely borne out. We think that few analysts will fail to keep this book upon their laboratory shelf.

**ELECTRO-CHEMICAL ANALYSIS.** BY EDGAR F. SMITH, PROFESSOR OF ANALYTICAL CHEMISTRY IN THE UNIVERSITY OF PENNSYLVANIA. PHILADELPHIA: P. BLAKESTON, SON AND CO., 1012, WALNUT STREET.

THIS little work includes within 116 pages a concise account of the application of electrolysis to chemical analysis. Commencing with an explanation of constants, batteries, and the general theory and practice of electrolysis, it takes up in succession (1) the estimation of metals, (2) the separation of metals, and (3) oxidation by the electric current. Any chemist wanting to see at a glance all that has been done in this ever-advancing branch of analysis up to date, will find the book easy to read, well expressed, and students will obtain by its perusal a good stock of general ideas on the subject.

**MICRO ORGANISMS, INCLUDING AN ACCOUNT OF RECENT EXPERIMENTS ON THE DESTRUCTION OF MICROBES IN CERTAIN INFECTIOUS DISEASES.** BY A. B. GRIFFITHS, Ph.D., F.R.S.E., F.C.S. LONDON: BAILLIERE, TINDALL AND COX, 20, KING WILLIAM STREET, STRAND.

ALTHOUGH, of course, a large portion of this book of 350 pages is specially written for medical men, yet there are parts intensely interesting to the public analyst, who is continually brought into contact with sanitary matters in assisting his medical officer with experimental help. The methods of bacteriological research are simply, yet clearly, laid out, and the illustrations of the microscopic appearances are drawn as they really appear, without the fantastic magnifications and exaggerations to which microscopists are so prone in published pictures, and which the unhappy reader, who does not possess a £25-apochromatic objective, generally fails to realise in practice. To medical men the book should simply be invaluable, being right up to date, and yet not so ponderous but that it can be easily digested in spare moments.

**UNTERSUCHUNGEN AUS DER PRAXIS DER GAHRUNGSINDUSTRIE.** BY DR. EMIL C. HANSEN, CARLSBERG, MUNICH, OLDENBOURG.

A SECOND and considerably enlarged edition of this notable work has just appeared. It is written for the practical brewer, and consequently treats the subject chiefly on its technical side, only so much theoretical matter being introduced as is necessary to render the subject intelligible. The process by which the small sample of yeast, grown in the laboratory from one single yeast cell, is increased into a quantity sufficient to carry out fermentation on a commercial scale, is minutely described, as is also the apparatus required for the process. By means of an apparatus of this kind, which by no means demands an immoderate outlay, the brewer is enabled to secure for himself a constant supply of identically the same yeast, an advantage to him almost inestimable. We note the continued extension of Dr. Hansen's process, which is now more or less used in every portion of the civilised globe, and has met with the most unqualified approval of many of the leading authorities on brewing matters both in this country and abroad.

#### CORRESPONDENCE.

*[The Editor is not in any way responsible for opinions expressed by his correspondents.]*  
To the Editor of the ANALYST.

DEAR SIR,—With reference to the modified Feleitmann test, using aluminium instead of zinc, attributed to Professor Johnson in the ANALYST of this month, you will find an account of the same modification in the *Chemical News* of April 18th, 1873, as published therein by myself.

Yours obediently,

J. W. GATEHOUSE.

36, Broad Street, Bath,  
December 4th, 1890.

# THE ANALYST.

FEBRUARY, 1891.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The annual meeting was held at Burlington House on Wednesday, the 14th January. The President, Mr. Adams, in the chair.

The minutes of the previous meeting were read and confirmed.

The report of the auditors (Messrs. Cassal and Harland), was read, showing a balance in hand of £114, besides arrears due, whereupon

Dr. MUTER moved, and it was carried unanimously, that the report be adopted and circulated among the members, and that another £100 be invested in Consols as soon as convenient.

Mr. Thomas Hughes, Public Analyst for Cardiff and Newport, was proposed as a member.

The President (Mr. Adams) then delivered his valedictory address as follows:—

GENTLEMEN,—In the first place allow me to wish you a Happy and Prosperous New Year.

This is, I believe, our 16th anniversary, and according to custom it is my duty to report to you the position of our Society, and in a brief manner to review the course of our proceedings during the year just expired.

We have on our rolls nine honorary members, 169 ordinary members, twenty-seven associates. Eleven new members and two associates were elected during the year, six have resigned, and we have suffered the loss of one other by death, namely, Dr. Henry Smith, Barrister-at-law and Public Analyst for Plumstead. He was a comparatively new member of much promise, and had he been spared might have become a useful and active one.

Financially our position is quite satisfactory. We have added a £100 to our

funded property, and still have a good balance at our bankers ; in point of fact we are some £63 richer now than at this time last year.

We have held eight ordinary meetings, and besides Committee meetings there have been eight meetings of Council.

The contributions to our transactions have included the following papers :—

| PAPERS IN 1890. |  |       | Author.                            |
|-----------------|--|-------|------------------------------------|
| Date.           |  |       |                                    |
| Jan. 8.         | " A Rapid Method of Estimating Quinine in Medicines "  | ..    | } Dr. Seaton and<br>H. D. Richmond |
| Feb. 12.        | " On the Composition of Milk and Milk Products "   | .. .. |                                    |
| "               | " On the Detection of Methylated Spirit in Sweet Spirits of Nitre "  | .. .. | Dr. Vieth                          |
| "               | " On the Detection of Cotton Seed Oil in Lard "  | .. .. | Dr. Muter                          |
| "               | " On the Solubility of Phosphate of Alumina in Acetic Acid "   | .. .. | } Dr. Muter and<br>L. de Koningh   |
| March 12.       | " On the Analysis of Disinfecting Powders Containing Commercial Carbolic and Sulphurous Acids "                          | .. .. |                                    |
| "               | " On the Chromate Test for Lead in Water "   | .. .. | W. C. Young                        |
| "               | " On the Determination of Rosin in Soap "  | .. .. | Dr. Muter                          |
| May 14.         | " Notes on the Bitter Principle of the Hop and Methods for Distinguishing Between it and the Bitter of Hop Substitutes " | .. .. | S. Harvey                          |
| June 11.        | " On some Recent Advances in our Knowledge of the Sugar Group "  | .. .. | R. Williams                        |
| "               | " On the Nitrogenous Constituents of Malt "  | .. .. | M. A. Adams                        |
| "               | " Some Points in the Analysis of Milk "  | .. .. | Dr. W. J. Sykes                    |
| "               | " Notes on the Chemistry and Detection of Certain Hop Substitutes "  | .. .. | Dr. W. J. Sykes                    |
| Nov. 12.        | " On Food Preservatives "  | .. .. | H. D. Richmond                     |
| "               | " On the Adulteration of Food with Boracic Acid "  | .. .. | } A. H. Allen and<br>W. Chattaway  |
| "               | " On the Detection and Estimation of Boracic Acid in Milk and Cream "  | .. .. |                                    |
| "               | " The Detection of Methylated Spirits in Tinctures, Spirits, or other Compounds "  | .. .. | Otto Hehner                        |
| Dec. 10.        | " On the Composition of Butter "   | .. .. | C. E. Cassal                       |
|                 |  |       | C. E. Cassal                       |
|                 |  |       | Dr. Ashby                          |
|                 |  |       | Dr. Vieth                          |

The country meeting, which was to have been held at Gloucester, was abandoned because too few names were sent in to give hope of a successful meeting. With this exception the ordinary meetings have been well attended and the discussions well sustained. The only remark I would venture under this head is the hope that in the future more of our younger members may be induced to contribute papers.

Of the matters that have engaged the attention of your Council, some have been of great importance, and perhaps that which is most important of all relates to the qualification that should be required of candidates for the office of public analyst. On more than one occasion it has come to the knowledge of the Council that persons inadequately qualified have been appointed. In some such cases it has been argued that because the district for which the appointment was made was small, and the payment for the work required was also small, it was impossible therefore to command the services of better qualified men. If not a mere evasion of the point at issue the folly and error of this argument is obvious. They proceed upon the assumption that the holder of an office of public analyst must of necessity reside within the district for which he is appointed.

Of course, if a duly qualified man can be found within the district, it is an advantage in many respects that he should be chosen. But in the alternative case, where such a man is not to be found, there seldom or never is much difficulty in obtaining the services of a well-qualified man in some neighbouring district able to execute the duties just as well as though he lived within the district.

But it is well known that there are other and more potent reasons that bring about these unsatisfactory appointments.

In small places it often happens that interested motives rule in the selection of the public analyst, some of the individual items constituting the appointing bodies not seldom being themselves the chief among the transgressors against the Food and Drugs Act, have an *unwholesome* fear of competent and independent officers, because, on their own personal accounts, they have so much reason to dread the efficient discharge of the functions of the public analyst.

With the object of preventing these unfit appointments, so injurious to the public interest and the reputation of our profession, your Council has memorialised the Local Government Board. Let us hope that the memorial may receive, not only due attention, but also that it may result in the promulgation of some definite regulations as to the minimum standard for education and credentials to be required of future candidates before confirmation of any appointment to the office of Public Analyst can be obtained of the Local Government Board.

This naturally leads to a consideration of the question—How is it possible in some cases for a local or the central authority to decide upon the qualifications of a hitherto untried man?

Our department of applied chemistry, during the last ten or fifteen years, has developed into a distinct specialty, and has attained so high a position as a technical art that none but those who have been trained to it can hope to be sufficiently proficient to be safely entrusted with the exercise of a public function which in incompetent hands is liable to deal mischief and injury broadcast. The best available remedy for this state of things would appear to be an examinational test, specifically designed to discover the practical knowledge of candidates in our own special department.

No such public test at present exists. It is not surprising that this necessity should have arisen; we find in other professions a similar necessity has arisen. In the profession of medicine, for instance, until within the last ten or fifteen years, hygiene, or State medicine, as it is called, had few followers and fewer teachers, and no organised examinations; now, this department has developed into a large and most important branch, with its separate schools, teachers, and examiners, and it is likely in the near future to rank higher in importance even than curative medicine. As a consequence, not only are men found to devote themselves specially to its cultivation and

practice, but also Parliament has deemed it necessary to impose special examinational tests as guarantees to the public that practitioners of state medicine shall be duly and specially qualified for its practice before they shall be permitted to undertake the duties of medical officer of health.

The case of the public analyst in all respects presents an exact parallel with that of the practitioner of public health ; the one is a State chemist and the other is a State physician, and both should be equally furnished with satisfactory credentials for fitness, each for their respective callings.

Turning to another matter, you will remember that at about this time last year an overture emanating from the Institute of Chemistry reached this Society, having for its object an amalgamation of our Society with that body. The scheme met with partial favour ; some thought advantage would accrue from such an arrangement, providing always that effective provision could be devised to safeguard the special interests and promote the special objects for which our Society exists ; some thought an amalgamation would strengthen our influence, support us in our dealings with public bodies, and give more weight to our counsel when applied for for legislative purposes, and that it would also provide a larger audience at our meetings, and, as a consequence, widen the interests and possibly increase the participation in our transactions. All most desirable objects in themselves. But some, on the other hand, mistrust any idea of amalgamation, fearing not only that such a course would fail of these purposes, but that it would also be fraught with serious risk of a complete destruction of the influence and advantages which, as a separate Society, we have built up for ourselves and now enjoy. They believe that if our small Society consented to sink its separate identity in the general mass of the members of the Institute of Chemistry, that we should lose all cohesion and concentration of purpose, and in the end become absorbed into a large and unsympathetic body that certainly might, and probably would, give but scant attention to our special labours or particular interests.

The negotiation, however, has not advanced beyond the preliminary stage of proposal, and if it has not by this time actually dropped out of consideration, certainly it has not gained ground during the past year.

If, however, the scheme should be resuscitated, it is important that all of us should bear in mind what, as public analysts, we owe to this Society, which has been our rallying-place, our workshop, and our recreation-ground ; where we have taken counsel of one another, and made many friendships ; where, to the immense advantage of our craft, we have contended in professional rivalry, but with personal amity ; where crude notions have been tested, and sometimes forged into valuable weapons ; where accumulated stores of knowledge have been stocked, and models for our future guidance welcomed as to a home. I say God speed to the Society ; may it go on and prosper, and inspire all of us

with a determination not to relax our hold one iota upon the profits, privileges, and pleasures it brings to us.

The scrutineers of the voting-papers then reported that the following gentleman had been elected as officers and Council for the year 1891 :—

PRESIDENT—Otto Mehner.

VICE-PRESIDENTS (who have filled the office of President)—M. A. Adams, F.R.C.S. ; A. H. Allen ; A. Dupré, Ph.D., F.R.S. ; C. Heisch ; Alfred Hill, M.D. ; J. Muter, Ph.D., M.A., F.R.S.E. (Who have not filled the office of President)—R. R. Tatlock, F.R.S.E. ; W. J. Sykes, M.D., D.Ph. ; P. Vieth, Ph.D.

TREASURER—C. W. Heaton.

HON. SECRETARIES—R. H. Davies ; Bernard Dyer, B.Sc.

OTHER MEMBERS OF COUNCIL—A. Ashby, M.B., F.R.C.S. ; T. P. Blunt, M.A. ; Sir Chas. Cameron, M.D., F.R.C.S. ; C. E. Cassal ; G. Embrey ; John Hughes ; T. Stevenson, M.D., F.R.C.P.

The names of those Members of Council whose term of office has not yet expired, and who consequently do not retire this year, are S. Harvey ; G. H. Ogston ; Boverton Redwood, F.R.S.E. ; E. Seaton, M.D., F.R.C.P. ; and E. W. Voelcker.

The following gentlemen were also reported to have been duly elected as members :—F. H. Perry Coste, F.C.S., Analyst, London ; Leo. Taylor, F.I.C., Analyst, Walthamstow.

Mr. ADAMS then said :—Before I resign this chair, gentlemen, to the worthy successor you have chosen to follow me, I heartily thank you one and all for the support and courtesy you have accorded to me during my two years of office.

Mr. HEHNER, having taken the chair as President, thanked the Society for the honour they had conferred upon him. He could only assure them, perhaps he need not assure them, that he should do his best to uphold the interests of the Society and its independence, and to be just and right to every member of it, so that when the time came for him to give up the chair to his successor, it should not be said that the position had suffered in his hands.

With regard to the future meetings of the Society, Mr. Mehner subsequently stated that in order to suit the convenience of the new secretary, Mr. Davies, the Council had arranged to hold them on the first Wednesday instead of the second in each month, with the exception of that in this month (February), which will be held on the 11th inst.

The President then moved, and it was unanimously carried, that a vote of

thanks be passed to the President and Council of the Chemical Society for the use of their rooms during the past year.

Mr. ALLEN having congratulated Mr. Hehner on his election, said he rose to move a vote of thanks to their retiring President, Mr. Adams, for the manner in which he had presided over them during the past year, and for the admirable and eloquent address he had given them. These addresses were exceedingly important, for they enabled the President to bring before the Society subjects which were very important, though not suitable for papers. He congratulated Mr. Adams on the able manner in which he had laid the various points in his address before them, and they would all read the address with great attention when they had the opportunity of seeing it in print. With respect to Mr. Adams's conduct in the chair, the speaker was sure they would agree with him that he had shown himself to be the right man in the right place, with his sauvity of manner and his power of showing, when necessary, that he could put his foot down, as he had done when he had to stop discursive discussion.

Dr. SYKES seconded the motion, which was carried unanimously, and Mr. Adams briefly returned thanks.

Mr. G. Embrey read the following paper :—" A Comparison of English and American Cider, with Suggestions for Estimating the Amount of Added Water."

The Annual Dinner was afterwards held at the Hotel Continental, Regent Street, when a large number of members and friends spent a very pleasant and convivial evening.

*(Conclusion of the Society's Proceedings.)*

## FURTHER NOTES UPON THE ANALYSIS AND COMPOSITION OF BUTTER-FAT.

By WILLIAM JOHNSTONE, Ph.D., F.I.C., F.C.S.

IN the June number of the ANALYST of 1889, I roughly described a method whereby the soluble and insoluble fatty acids of a butter-fat could easily be determined with accuracy, and since the publication of that paper the correctness of the process has been confirmed by the independent researches of Messrs. Bondzynski and Rufie, and recorded by them in the *Zeitschr. Annal. Chem.* (29·1·6').

Since the publication of my previous paper I have introduced several improvements in the various manipulations, and the process is now carried out as follows :—

The butter-fat is carefully clarified and saponified with a known quantity of standard alkali. The saponification is carried out in the following manner. Instead of saponifying in a closed flask as previously stated, and which required to be repeatedly shaken, I now carefully weigh out 2·5 grams. into a stout glass tube with flat bottom

(7 inches high and  $2\frac{1}{2}$  inches wide), practically a narrow, strong beaker, then add 2 ozs. of 95 per cent. neutral alcohol and 1 oz. of ether, and finally run in 25 c.c. of  $\frac{N}{NaHO}$

solution, attach the tube to an upright condenser, and heat by means of a water-bath until saponification takes place, the time generally required being about one hour. When saponification is complete, the tube is removed from the condenser, 3 oz. of proof spirit added, and the titration immediately commenced, using phenolphthalein as an indicator, the temperature of the soap solution being maintained at a temperature of between  $80^{\circ}$  and  $95^{\circ}$  F., the following being the actual figures obtained in three duplicate analysis operating in the above-described manner :—

| Fat taken                           | I.<br>2.5    |              | II.<br>2.5   |              | Beef fat.<br>2.5 |              |
|-------------------------------------|--------------|--------------|--------------|--------------|------------------|--------------|
| $\frac{N}{NaHO}$ added              | 25.00        | 25.00        | 25.00        | 25.00        | 25.00            | 25.00        |
| $\frac{N}{H_2SO_4}$ added           | 12.00        | 12.00        | 12.00        | 12.00        | 12.00            | 12.00        |
| $\frac{N}{NaHO}$ consumed           | 13.00        | 13.00        | 13.00        | 13.00        | 13.00            | 13.00        |
| Acid required to complete titration |              |              |              |              |                  |              |
| $\frac{N}{10H_2SO_4}$               | 14.90 = 1.49 | 15.00 = 1.50 | 10.90 = 1.09 | 10.60 = 1.06 | 24.60 = 2.46     | 24.30 = 2.43 |
| Total $\frac{N}{NaHO}$ consumed     | 11.51        | 11.50        | 11.91        | 11.94        | 10.54            | 10.57        |
| Average                             | 11.50        |              | 11.92        |              | 10.56            |              |

Working in this manner, an accurate estimation of the amount of alkali required for saponification is obtained, and from which the Koettstorfer number of the fat is readily calculated. The titration of the alcoholic soap solution requires, as stated, to be made at a temperature of between  $80^{\circ}$  and  $90^{\circ}$ , otherwise results are obtained which at present I do not venture to account for, but simply record them until I have time to fully investigate the cause, as it is apparently not due to dissociation as is ordinarily accepted, as otherwise we should have more alkali consumed at  $90^{\circ}$  F. than at  $60^{\circ}$  F., whereas we have more consumed at  $60^{\circ}$  F. than at  $90^{\circ}$  F. Thus :—

| Butter-fat taken  | 2.5 grms.   |             | 2.5 grms.   |             |
|---|-------------|-------------|-------------|-------------|
| Alkali taken $\frac{N}{NaHO}$                             | 25.00       | 25.00       | 25.00       | 25.00       |
| Acid added $\frac{N}{H_2SO_4}$                            | 12.00       | 12.00       | 12.00       | 12.00       |
| Acid required to complete titration $\frac{N}{10H_2SO_4}$ | 13.00       | 13.00       | 13.00       | 13.00       |
| Total alkali consumed at $60^{\circ}$ F. . . . .          | 6.20 = 0.62 | 6.50 = 0.65 | 6.40 = 0.64 | 6.60 = 0.66 |
|   | 12.38       | 12.35       | 12.36       | 12.34       |

The above, upon standing a few minutes, begin to show alkaline reaction, and deposit a precipitate of fatty acids, the solution at the same time evolving a continuous stream of small bubbles; if the solutions are now heated in the water-bath to a tem-



perature of 90° F., the precipitate that has formed redissolves, and the following quantity of acid is required to again render the solution neutral, which, upon standing any length of time, remains clear and also neutral.

|  |                             |                             |                             |                             |
|--|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Total alkali required at 60° F.                | 12.38                       | 12.35                       | 12.36                       | 12.34                       |
| Acid required at 90° F. $10 \frac{N}{H_2SO_4}$ | $3.42 = \frac{0.34}{12.04}$ | $3.20 = \frac{0.32}{12.03}$ | $3.20 = \frac{0.32}{12.04}$ | $3.30 = \frac{0.33}{12.01}$ |
| Average of $\frac{N}{NaHO}$ at 60° F.          |                             | 12.03                       |                             | 12.02                       |
| “ “ $\frac{N}{NaHO}$ at 90° F.                 |                             | 11.92                       |                             | 11.92                       |
| Difference between the two estimations . . . . |                             | .10                         |                             | .10                         |

Beef-fat, or similar triglycerides, do not behave in the above-described manner.

After the titration is completed, the alcoholic soap solution is carefully washed into a porcelain basin, the alcohol evaporated off, excess of acid added so as to decompose the soap, then gently heated until the fatty acids are melted.

The insoluble fatty acids are now filtered off through an unweighed filter in the usual manner, thoroughly washed with boiling water until the washings are neutral, when the filter containing them is set aside in a moderately warm place and allowed to air dry. When the filter is sufficiently dry, it is transferred to a Soxhlet extraction-tube, and thoroughly extracted with *dry ether*, the acids being received in an accurately-weighed flask of sufficient capacity, so as to allow the ultimate titration of the insoluble fatty acids to be made in the same flask; the washing out of the insoluble fatty acids with alcohol from the extraction-flask now becomes unnecessary. When the extraction is complete, the ether is evaporated off, and the flask and contents are placed in the water-oven, and when dry, allowed to cool and finally weighed. Thus:—

|                                 |         |         |         |         |         |         |
|---------------------------------|---------|---------|---------|---------|---------|---------|
| Insoluble fatty acids and flask | 32.4376 | 28.3180 | 32.4500 | 29.0433 | 27.3704 | 29.5244 |
| Flask . . . .                   | 30.2942 | 26.1744 | 30.2948 | 26.8856 | 25.0144 | 27.1613 |
| Insoluble fatty acids of        |         |         |         |         |         |         |
| 2.5 grms. . . .                 | 2.1434  | 2.1436  | 2.1552  | 2.1577  | 2.3560  | 2.3631  |
| + 40 = per cent. . . .          | 85.736  | 85.744  | 86.208  | 86.308  | 94.240  | 94.524  |
| Average . . . .                 | 85.74   |         | 86.25   |         | 94.38   |         |

When the percentage of insoluble fatty acids have been ascertained, add sufficient normal alkali to the flask, heat gently, when saponification rapidly takes place; then add 3 oz. of 85 per cent. alcohol, and titrate again with standard acid, and estimate the amount of alkali now consumed by the insoluble fatty acids, from which the Koettstofer number of the insoluble fatty acids can be calculated. Thus:—

|                              |                            |                            |                             |                             |                              |                              |
|------------------------------|----------------------------|----------------------------|-----------------------------|-----------------------------|------------------------------|------------------------------|
| $\frac{N}{NaHO}$ taken       | 12.00                      | 12.00                      | 12.00                       | 12.00                       | 12.00                        | 12.00                        |
| $\frac{N}{H_2SO_4}$ required | $38.0 = \frac{3.80}{8.20}$ | $38.4 = \frac{3.84}{8.16}$ | $34.60 = \frac{3.46}{8.54}$ | $33.60 = \frac{3.36}{8.64}$ | $14.54 = \frac{1.45}{10.55}$ | $14.70 = \frac{1.47}{10.53}$ |
| Average                      | 8.18                       |                            | 8.59                        |                             | 10.54                        |                              |

| Then                 |  |                     |                     |                     |                     |                       |                       |
|----------------------|--|---------------------|---------------------|---------------------|---------------------|-----------------------|-----------------------|
| $\frac{N}{NaHO}$     | consumed by 2.5 grms. butter   | 11.51               | 11.50               | 11.91               | 11.94               | 10.54                 | 10.57                 |
| $\frac{N}{NaHO}$     | " by fatty acids   | $\frac{8.20}{3.31}$ | $\frac{8.16}{3.34}$ | $\frac{8.54}{3.37}$ | $\frac{8.64}{3.30}$ | $\frac{10.55}{.01 +}$ | $\frac{10.53}{.04 -}$ |
| Average,             |  | 3.32                |                     | 3.33                |                     | 0.02                  |                       |
| $\frac{N}{NaHO}$     | required by soluble fatty acids of 2.5 grms. of butter-fat calculated into $C_4H_8O_2$ . |                     |                     |                     |                     |                       |                       |
|                      |  | 11.651              | 11.756              | 11.776              | 11.616              |                       |                       |
| Average, $C_4H_8O_2$ |  | 11.70               |                     | 11.69               |                     |                       |                       |

Working in the manner indicated, we obtain an accurate estimation of the total soluble and insoluble fatty acids contained in a butter-fat; as the accuracy of Koettstorfer's process has never been questioned, it stands to reason that if the saponification number can be accurately determined in the original fat, it can also be accurately determined in the insoluble fatty acid, and any difference between these two determinations must be due to soluble fatty acids.

The process as described is simple, rapid and accurate, only requiring ordinary care: No complicated apparatus or delicate reagents are necessary, such as those required for the Reichert Wollny process—a process which has been described by Mr. Otto Hehner (now the President of the Society of Public Analysts) as follows:—"Whatever comparative results Reichert's process was capable of furnishing, if always performed in the same manner. Yet analysts should not on principle tolerate a process by which only a portion of the substance to be estimated was obtained; but in all cases where a real and accurate estimation was possible, such rough and ready methods should not be admitted by careful analysts." In my previous paper I expressed some doubts as to the nature of the soluble volatile fatty acids; but from the results obtained in the following experiment all doubts in my mind upon that point has now been removed. Considerably over one pound of butter-fat was saponified with NaHO, the resulting soap decomposed, and the soluble fatty acids again neutralised with NaHO (after the separation of the insoluble fatty acids had been accomplished), and evaporated to crystallisation, the glycerine drained off, the salts redissolved in water and recrystallised, the crystals obtained being washed with a mixture of alcohol and ether (two parts of 90 per cent. alcohol and one part of ether) to remove any adhering glycerine and water, and then air-dried.

The purified crystals were then placed in a retort, water added to dissolve them, and finally  $H_2SO_4$  added, and distillation conducted by means of an oil bath, until vapours of  $H_2SO_4$  began to appear in the retort.

The distillate obtained was neutralised by  $BaH_2O_2$  solution, and then a current of  $CO_2$  passed through the solution, which was afterwards heated, and finally filtered. A portion of the liquid was then evaporated on the water-bath, to dryness, and finally dried at  $260^\circ F.$ , thus—

|   |        |         |
|---|--------|---------|
| Barium salt dried at $260^\circ F.$ + Basin | ...    | 40.2200 |
| Basin                                       | ... .. | 39.8278 |
| Amount of barium salt taken                 | ... .. | .3922   |

Redissolved in water and evaporated with dilute  $H_2SO_4$ , and again evaporated to dryness, and igniting gave

|   |     |     |     |     |                          |
|---|-----|-----|-----|-----|--------------------------|
| Basin + $BaSO_4$                              | ... | ... | ... | ... | 40.1224                  |
| Basin ...                                     | ... | ... | ... | ... | 39.8276                  |
| $BaSO_4$                                      | ... | ... | ... | ... | 2946                     |
| A 100 parts of the above barium salt yielding |     |     |     |     | 75.19 per cent. $BaSO_4$ |
| A 100 ,, $Ba(C_4H_7O_2)_2$ ,,                 |     |     |     |     | 74.92 per cent. $BaSO_4$ |

Further research in this direction was not continued.

The glycerine and mother liquor obtained in purifying the barium salt was now examined for the possibility of it still containing a soluble non-volatile fatty acid, but with negative results, as far as the investigation in this direction was carried.

I now directed my attention to the volatile fat acid which collects in the condenser when a Reichert Wollny test is being made. Some of the fat thus collected was dissolved in 95 per cent. neutral alcohol, and then carefully neutralised with an alcoholic solution of  $BaH_2O_3$ , which caused a heavy white precipitate which was filtered off from the solution it was formed in, then carefully washed with alcohol and ether, and finally dried over sulphuric acid.

A portion of the barium salt thus formed was taken and dissolved in dilute sulphuric acid, and evaporated to dryness in the water-bath, ignited and weighed, which gave the following results :—

|  |   |       |
|--|---|-------|
| Amount of barium salt taken                      | = | .2525 |
| Weight of $BaSO_4$ produced from amount taken    |   | .1222 |
| A 100 parts of above barium salt yields $BaSO_4$ |   | 48.39 |
| A 100 ,, ,, $Ba(C_{10}H_{19}O_2)_2$ ,, $BaSO_4$  |   | 48.64 |

Consequently the above result proves the fat collected in the condenser consists mostly of capric acid.

The results of the analysis of the two butters as given in this paper were obtained from June butters ; the first was received from Norfolk, the second from Ireland.

The insoluble fatty acids in both instances being the lowest I had ever obtained with correspondingly high soluble fatty acids, as butyric acid, and at the same time giving results unaccountable when reviewed as follows, I determined, if possible, to secure more of the butter for further examination, as there was no doubt whatever as to their genuineness, both samples being from private country dairies, the cows not being kept, in a commercial point of view, more than for domestic consumption of large private establishments.

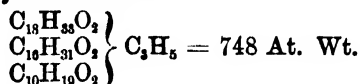
|                       |     |     |     |        |        |
|-----------------------|-----|-----|-----|--------|--------|
| Insoluble fatty acids | ... | ... | ... | 85.74  | 86.25  |
| Butyric acid...       | ... | ... | ... | 11.82  | 11.69  |
| Glyceryl              | ... | ... | ... | 5.82   | 6.03   |
|                       |     |     |     | 103.38 | 103.97 |

The above figures, however, are not correct as regards the glyceryl, as the glycerine has been very carefully estimated in duplicate by the well-known method of Messrs. Benedikt and Zsigmondy, and gave the following results :—

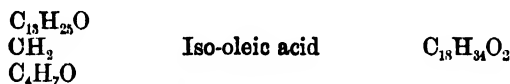
|                      |       |       |       |       |
|----------------------|-------|-------|-------|-------|
| $C_3H_5O_3$          | 12.08 | 12.23 | 12.24 | 12.19 |
| $= C_3H_5$           | 4.98  | 5.05  | 5.05  | 5.03  |
| Average for $C_3H_5$ | 5.01  |       |       | 5.04  |

proving that the glyceryl cannot be correctly calculated in a butter-fat from its saponification equivalent.

I am now engaged upon the examination of the insoluble fatty acids when pressure of outside business does not interfere with same, and the results already obtained suggest to my mind the following explanation, namely, that there are two kinds of butter, one a compound tri-glyceride, giving insoluble fatty acids as low as 85·81 per cent., and one a mixture of two compound tri-glycerides, giving insoluble fatty acids up to 90 per cent. The first may be represented by this formula :—



Iso-oleo-palmito-capriate of glycerine the first radicle having the following constitution :—

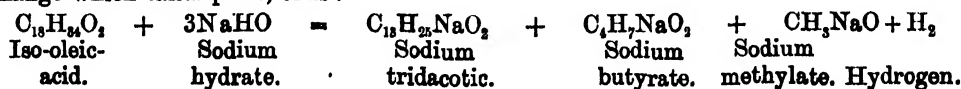


The iso-oleo-palmito-capriate of glycerine may be represented as follows :—

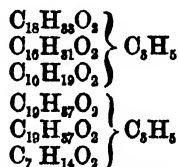
| Theory.                              |             |                | Theory.                                |              | Found. |
|--------------------------------------|-------------|----------------|--|--------------|--------|
| $\text{C}_{13}\text{H}_{25}\text{O}$ | 26·33       |                | $\text{C}_{13}\text{H}_{25}\text{O}_2$ | 28·60        |        |
| $\text{CH}$                          | 1·73        |                | $\text{CH}_4 ?$                        | 2·13         |        |
| $\text{C}_4\text{H}_7\text{O}$       | 9·49        | yields upon    | $\text{C}_7\text{H}_8\text{O}_2$       | 11·76        | 11·70  |
| $\text{C}_{16}\text{H}_{31}\text{O}$ | 34·09       | saponification | $\text{C}_{16}\text{H}_{33}\text{O}_2$ | 34·22        |        |
| $\text{C}_{10}\text{H}_{19}\text{O}$ | 22·86       |                | $\text{C}_{10}\text{H}_{20}\text{O}_2$ | 22·99        |        |
| $\text{C}_3\text{H}_5$               | 5·47        |                | $\text{C}_3\text{H}_8\text{O}_2$       | 12·30        | 12·23  |
|                                      | <hr/> 99·97 |                |  | <hr/> 112·00 |        |

From the above formula it will be at once apparent that I am assuming that a butter-fat yielding 85·81 per cent. of insoluble fatty acids is a tri-glyceride wherein the first radicle of the tri-acid compound is a compound acid of the formula  $\left. \begin{array}{l} \text{C}_{13}\text{H}_{25}\text{O} \\ \text{C}_4\text{H}_7\text{O} \end{array} \right\} \text{CH}_2$  (iso-oleic-acid ?) tridecatoic methane butyrate, the second radicle being palmitic acid, and the third radicle capric acid, forming a molecule of butter-fat.

When a compound such as tridecatoic methane butyrate is saponified with an alkali in 95 per cent. alcohol, the following equation may be taken as representing the change which takes place, thus :—



The second butter spoken of is a mixture of the above tri-glycerine with tri-nondecatoic acid. Thus :—



Of course, I advance the above theory with all due reservation, but from the results obtained I think I am warranted in advancing it, the correctness of which, of

course, will be proved when a closer examination of the insoluble fatty acids have been made an investigation, which I have now well in hand, and the results already obtained in that direction are so far favourable to supporting it. The two samples of butter-fat at present under examination are so very much alike in composition that I shall now draw your attention to the three samples of butter-fat mentioned in the June number of the ANALYST of 1889, and then the difference between these samples when viewed by this theory immediately became apparent. If the  $C_4H_7O_2$  found is calculated into the iso-oleo-palmito-capriate of glycerine we get the following results:—

| Thus in sample              | A.     | Fatty acids. | W.     | Fatty acids. | Y.     | Fatty acids. |
|-----------------------------|--------|--------------|--------|--------------|--------|--------------|
| Iso-oleo-palmito-capriate   | 62.47  | 53.61        | 53.21  | 45.66        | 65.19  | 55.95        |
| of glycerine                |        |              |        |              |        |              |
| $(C_{19}H_{37}O_2)_3C_8H_5$ | 37.53  | 36.00        | 46.79  | 44.88        | 34.81  | 33.39        |
|                             | 100.00 | 89.61        | 100.00 | 90.54        | 100.00 | 89.34        |
| Fatty acids actually found  |        | 89.95        |        | 90.00        |        | 89.83        |

It now becomes apparent that the radicle of œnanthylic acid might replace one of nondecaic acid in the tri-glyceride, and form the di-nondecaic œnanthylic of glycerine, which apparently is the case in sample marked W, for when calculated as di-nondecaic œnanthylic the insoluble fatty acids came to 90.12 against 90.00 found; a result well within the limit of error, as the process has been rendered more accurate since the temperature was taken into consideration, and which was previously not considered of so much importance. The difference between the amount of iso-oleo-palmito-capriate of glyceride and 100 I put down as tri-glyceride of nondecaic acid (as I have results which point to such being the case) the following peculiarity will be observed, namely, that starting with butyric acid we have every fourth acid of the series in butter-fat up to nondecaic.

In concluding this paper, I add the following detail, obtained from the butters mentioned in this investigation, so that they may be also put on record:—

|                                 | A.     | W.     | Y.     | I.     | II.    |
|---------------------------------|--------|--------|--------|--------|--------|
| Sp. gr. at 37.8°C .. ..         | 907.80 | 904.74 | 906.63 | 913.85 | 912.96 |
| Melting point .. ..             | 36.5°C | 36.5°C | 36.0°C | 30.8°C | 31.2°C |
| Sp. gr. fatty acid at 15.5°C .. | 96335  | 96349  | 96325  | 797.58 | 797.66 |
| Melting point fatty acids ..    | 41.5°C | 41.5°C | 41.0°C | 38.3°C | 38.5°C |

Since writing the above an unexpected confirmation of the amount of butyric acid contained in a butter yielding 85.80 per cent. of insoluble fatty acids has turned up.

I find from my laboratory note-book that on the 3rd February, 1887, I received a sample of butter which gave 85.80 per cent. of insoluble fatty acids, and had the following specific gravity and melting point:—

|                   |        |                |         |
|-------------------|--------|----------------|---------|
| Sp. gr. at 37.8°C | 913.83 | Melting point. | 29.4°C. |
|-------------------|--------|----------------|---------|

A portion of this butter, 3.9971 grams., were saponified with lime in a flask, 100 c.c. of water containing phosphoric acid added, and then 500 c.c. of water, and then 500 c.c. distilled. The addition of the 500 c.c. and distillation was repeated five consecutive times, the last 200 c.c. coming over perfectly neutral; the various distillates were then titrated, and gave volatile acid calculated as  $C_4H_7O_2$ .

|   |            |        |
|---|------------|--------|
| 1 | Distillate | 3.845  |
| 2 | "          | 3.192  |
| 3 | "          | 2.425  |
| 4 | "          | 1.210. |
| 5 | "          | 1.100  |

Total  $C_4H_7O_2$  11.772 against theoretical 7.76

The subject is one which has up to the present been beset with great difficulties, so I have ventured to record a few preliminary results, for if I might so write this investigation is merely in its infancy; a large amount of tedious and laborious work will require to be undertaken before I can thoroughly establish the correctness of my theory, consequently I have been induced to advance the same in its embryo in the hope that others with more leisure than myself may be enticed to investigate the subject in the direction indicated, and help to solve the question of butter analysis, as it certainly is in a most unsatisfactory state at present.

## STUDY OF A METHOD FOR THE QUANTITATIVE DETERMINATION OF SUCROSE, INVERT-SUGAR AND DEXTROSE, OR LEVULOSE.

BY F. G. WIECHMANN, PH.D.

(Concluded from page 19.)

The dextrose used in the following experiments was anhydrous crystallised dextrose, prepared under the Behr patent.

The levulose was prepared under the writer's directions in the following manner:

|                                |         |             |
|--------------------------------|---------|-------------|
| Inulin .. .. .                 | .. .. . | 18 grammes. |
| Sulphuric Acid (sp. gr. 1.840) | .. .. . | 36 cc.      |
| Water .. .. .                  | .. .. . | 516 „       |

This solution was set aside for nine days, then just neutralised with barium hydrate, filtered, and the filtrate evaporated to a solution having a density of 1.0043.

The levulose solution was examined by the polariscope, and tested with Fehling's solution, and was found by both tests to possess the properties of chemically-pure levulose.

The invert-sugar solution was prepared by dissolving 13.024 grammes of chemically-pure sugar (sucrose) in about 75 c.c. water, adding 5 c.c. hydrochloric acid, and heating in a water-bath up to between 67° C. and 70° C. When the contents of the flask had attained this temperature, they were kept at this point for five minutes more, with frequent agitation. Then the contents of the flask, after having been cooled down to 17.5° C., were made up to 100 c.c. with distilled water.

Fifty c.c. of this solution were removed, placed in a litre flask and made up to 1000 c.c.

Twenty-five c.c. of this solution correspond to 0.1628 gramme dry substance.

This amount, or whatever amount be taken for the analytical determination, must, before mixing with the copper solution, be neutralised by a solution of sodium carbonate, which is prepared by dissolving 1.7 grammes of the anhydrous salt in 1 litre of water.

A preliminary test made of the Sieben process on pure invert-sugar was the following:

Placed 25.0 grammes granulated sugar in 1 litre of water. Of this solution took 50 c.c., added 5 c.c. concentrated hydrochloric acid and made up to 100 c.c. Heated for five minutes between 67° and 69° C., cooled, neutralised with sodium carbonate, and made up to 500 c.c. Of this solution 5 c.c. = 0.125 grammes dry substance were used for the determination.

|   |               |
|---|---------------|
| This gave before Sieben's treatment .. ..                         | 0.243 copper. |
| Copper that should have been found after Sieben's treatment .. .. | 0.1215        |
| Copper found .. ..  | 0.1200        |

## EXPERIMENT I.

Determinations made :

1. Invert-sugar separately.
2. Anhydrous dextrose separately.
3. Mixture of invert-sugar and dextrose in *known* proportions.
4. Mixture of invert-sugar and dextrose, after Sieben's treatment.

1. Took 13.024 grammes chemically-pure sugar, dissolved in 100 c.c. flask, inverted with 5 c.c. HCl (German Government Method). Fifty c.c. of the inverted solution were made up to 1000 c.c. Twenty-five c.c. of this solution equal 0.1628 grammes dry substance. This was neutralised with  $\text{Na}_2\text{CO}_3$ , and the invert-sugar determined by the copper-test.

Result .. .. 0.311 gramme Cu.

2. 12.5 grammes anhydrous dextrose were dissolved up to 500 c.c. water. Ten c.c. of this solution, corresponding to 0.25 gramme dry substance, were used for the copper determination.

This determination was made three times.

|                                    |             |
|------------------------------------|-------------|
| Results: Determination No. 1 .. .. | = 0.473 Cu. |
| "      "      2 .. ..              | = 0.473 "   |
| "      "      3 .. ..              | = 0.475 "   |

3. Two hundred c.c. of solution No. 1 (= 1.3024 grammes dry substance) were mixed with 80 c.c. of solution No. 2 (= 2.000 grammes dry substance). Of this mixture, 35 c.c. were taken for the copper determination. These 35 c.c. represent, of solution No. 1, 25 c.c. (= 0.1628 gramme dry substance), and, of solution No. 2, 10 c.c. (= 0.2500 gramme dry substance).

Hence, if this mixture of invert-sugar and dextrose should reduce copper in the *same* proportion as these sugars do separately, the amount of Cu reduced here should be equal to the sum of the copper reduced by determination No. 1 + determination No. 2 given above, and equal to 0.784 gramme Cu. This determination was also made three times. By two minutes' boiling there were found:

|                                    |                    |
|------------------------------------|--------------------|
| Results: Determination No. 1 .. .. | = 0.764 gramme Cu. |
| "      "      2 .. ..              | = 0.769 " "        |
| "      "      3 .. ..              | = 0.772 " "        |

Repeating this experiment once more, but boiling for *three* minutes, there were found 0.775 gramme Cu.

4. Took, of solution No. 3, 212 c.c. (= 2.5 grammes dry substance). Heated for three hours with 60 c.c. six times normal strength HCl, cooled, neutralised with six times normal strength sodium hydrate, made up to 500 c.c., and used 50 c.c. of this solution (= 0.25 gramme dry substance) for the copper determination.

These 50 c.c. consisted of :

|                                    |                  |
|------------------------------------|------------------|
| Invert-sugar .. ..                 | 0.09861 grammes. |
| Dextrose .. ..                     | 0.15143 "        |
| 0.09861 invert-sugar reduces .. .. | 0.188 Cu.        |
| 0.15143 dextrose reduces .. ..     | 0.286 "          |

One-half of the invert-sugar is dextrose ; hence we should *expect* a yield of :

$$0.188 \div 2 = 0.094 \text{ Cu.}$$

$$0.286 \text{ ,,}$$

0.380

and there *were* found :

$$\text{Cu} = 0.3826 \text{ grammes.}$$

#### EXPERIMENT II.

Determinations made :

1. Invert-sugar.
2. Levulose separately.
3. Mixture of invert-sugar and levulose in known proportions.
4. Mixture of invert-sugar and levulose as in No. 3, after Sieben's treatment.

1. Proceeded exactly as in No. 1 (Experiment I.) and found as there : Result = 0.311 Cu.

2. 10 c.c. of a levulose solution equal to 0.180 grammes dry substance reduced .. .. 0.275 grammes Cu.

3. Used 250 c.c. of Solution 1 = 1.628 grammes dry substance and 100 c.c. of Solution 2 = 1.8 grammes dry substance (of which 93.3 per cent. are levulose), or levulose = 1.6794 grammes.

Of this mixture took 35 c.c.; these contained: 0.1628 grammes invert-sugar (which is the dry substance of Solution No. 1), and 0.1679 grammes levulose (which is the dry substance of Solution No. 2).

These together *should* reduce copper .. .. 0.586

The 0.1628 invert-sugar = 0.311 Cu.

The 0.1679 levulose = 0.275 Cu.

0.586

There *were* found : 0.5868 grammes Cu.

#### EXPERIMENT III.

Determinations made :

1. Mixture of sucrose, invert-sugar and dextrose.
2. Mixture of invert-sugar and dextrose.
3. Total dextrose in No. 1, after Sieben's treatment.

Test No. 1.

|        |                               |       | Cu reduced.     |
|--------|-------------------------------|-------|-----------------|
| Used : | Sucrose 0.26048 grammes       | .. .. | 0.4975 grammes. |
| "      | Invert-sugar 0.013024 grammes | .. .. | 0.0249 "        |
| "      | Dextrose * 0.0052096          | .. .. | 0.0095 "        |

Solution No. 1.—Copper reduced by :

|                  |       |        |
|------------------|-------|--------|
| Inverted sucrose | .. .. | 0.4975 |
| Invert-sugar     | .. .. | 0.0249 |
| Dextrose         | .. .. | 0.0095 |

0.5319 Cu.

\* Anhydrous crystalline dextrose.



*Solution No. 2.*—Copper reduced by :

|              |    |    |    |    |            |
|--------------|----|----|----|----|------------|
| Invert-sugar | .. | .. | .. | .. | 0 0249     |
| Dextrose     | .. | .. | .. | .. | 0·0095     |
|              |    |    |    |    | <hr/>      |
|              |    |    |    |    | 0·0344 Cu. |

*Solution No. 3.*—Copper reduced by dextrose, after

|                       |    |    |    |    |    |           |
|-----------------------|----|----|----|----|----|-----------|
| Sieben's treatment .. | .. | .. | .. | .. | .. | 0 269 Cu. |
|-----------------------|----|----|----|----|----|-----------|

*Calculation.*

|            |    |    |    |    |                     |
|------------|----|----|----|----|---------------------|
| No. 1      | .. | .. | .. | .. | 0·5319              |
| Less No. 2 | .. | .. | .. | .. | 0·0344              |
|            |    |    |    |    | <hr/>               |
|            |    |    |    |    | 0 4975 ÷ 2 = 0·2487 |
| No. 3      | .. | .. | .. | .. | 0 2690              |
| Less       | .. | .. | .. | .. | 0·2487              |
|            |    |    |    |    | <hr/>               |
|            |    |    |    |    | 0·0203 × 2 = 0·0406 |

This value 0 0406 is greater than No. 2 ; hence there is free dextrose present.

|       |    |    |    |    |                     |
|-------|----|----|----|----|---------------------|
| No. 2 | .. | .. | .. | .. | 0·0344              |
| Less  | .. | .. | .. | .. | 0 0203              |
|       |    |    |    |    | <hr/>               |
|       |    |    |    |    | 0 0141 × 2 = 0·0282 |

|       |    |    |    |        |
|-------|----|----|----|--------|
| No. 2 | .. | .. | .. | 0·0344 |
| Less  | .. | .. | .. | 0·0282 |
|       |    |    |    | <hr/>  |

0 0062 Cu due to free dextrose.

|   |          |
|---|----------|
| .. Cu due to free dextrose placed in the solution | = 0·0095 |
| .. Cu due to free dextrose, found                 | = 0·0062 |
| <hr/>   |          |

Difference = 0·0033

The difference is equal to only 3·3 milligrammes, but as such small quantities were worked with, the percentage of error is too great. This experiment was, therefore, repeated, but greater amounts of substance were used.

*Test No. 2.*

|                |          |    |    |    |    |             |
|----------------|----------|----|----|----|----|-------------|
| Used : Sucrose | 0·26048  | .. | .. | .. | .. | Cu reduced. |
| " Invert-sugar | 0·026048 | .. | .. | .. | .. | = 0·4975    |
| " Dextrose     | 0·013024 | .. | .. | .. | .. | = 0·04975   |
|                |          |    |    |    | .. | = 0·0246    |

*Solution No. 1.*—Cu reduced by :

|                  |    |    |    |    |    |         |
|------------------|----|----|----|----|----|---------|
| Inverted sucrose | .. | .. | .. | .. | .. | 0·4975  |
| Invert-sugar     | .. | .. | .. | .. | .. | 0·04975 |
| Dextrose         | .. | .. | .. | .. | .. | 0·0246  |

0·57185 Cu.

*Solution No. 2.*—Cu reduced by :

|              |    |    |    |    |    |         |
|--------------|----|----|----|----|----|---------|
| Invert sugar | .. | .. | .. | .. | .. | 0·04975 |
| Dextrose     | .. | .. | .. | .. | .. | 0·0246  |

0·07435 Cu.

*Solution No. 3.*—Cu reduced by dextrose after Sieben's treatment

0·2968 Cu.

## Calculation.

|                    |                     |
|--------------------|---------------------|
| No. 1 .. .. .      | 0.57185             |
| Less No. 2 .. .. . | 0.07435             |
|                    | <hr/>               |
|                    | 0.49750 ÷ = 20.2487 |

|               |        |
|---------------|--------|
| No. 3 .. .. . | 0.2968 |
| Less .. .. .  | 0.2487 |

$$0.0481 \times = 20.0962$$

This value, 0.0962, is greater than No. 2; hence free dextrose is present.

|               |         |
|---------------|---------|
| No. 2 .. .. . | 0.07435 |
| Less .. .. .  | 0.01810 |

$$0.02625 \times = 20.05250$$

|               |         |
|---------------|---------|
| No. 2 .. .. . | 0.07435 |
| Less .. .. .  | 0.05250 |

|  |                                  |
|--|----------------------------------|
|  | 0.02185 Cu due to free dextrose. |
| Cu due to free dextrose placed in the solution .. .. . | = 0.02460                        |
| Cu due to free dextrose found .. .. .                  | = 0.02185                        |
|  | <hr/>                            |
| Difference .. .. .                                     | = 0.00275                        |

The difference is equal to 2.75 milligrammes; whereas in the first test only 65.3 per cent. of the added dextrose was found, in this test 88.8 per cent. were recovered. As the differences encountered have never exceeded 3.5 milligrammes of copper, and have generally fallen below that figure, it is probable that working with larger amounts will decrease materially the percentage of loss.

## EXPERIMENT IV.

Determinations made:

1. Mixture of sucrose, invert-sugar and levulose in known proportions.
2. Mixture of invert-sugar and levulose.
3. Total dextrose in No. 1, after Sieben's treatment.

|                          |           |
|--------------------------|-----------|
| 1. Used: Sucrose .. .. . | 0.1628    |
| „ Invert-sugar .. .. .   | 0.01628   |
| „ Levulose .. .. .       | 0.0107415 |
|                          | <hr/>     |
|                          | 0.1898215 |

This should have reduced copper:

|                          |        |
|--------------------------|--------|
| Inverted sucrose .. .. . | 0.3110 |
| Invert-sugar .. .. .     | 0.0311 |
| Levulose .. .. .         | 0.0088 |

0.3509 Cu.

There were found in Test 1, 0.3572 Cu; in test 2, 0.3550 Cu. Calculating over to 0.25 gramme dry substance there should have been reduced .. .. 0.4625 copper.

There were found on 0.25 gramme dry substance:

Test 1, 0.4704 Cu.

Test 2, 0.4675 Cu.

|                       |    |    |    |    |           |
|-----------------------|----|----|----|----|-----------|
| 2. Used: Invert-sugar | .. | .. | .. | .. | 0.01628   |
| „ Levulose            | .. | .. | .. | .. | 0.0107415 |

0.0270215

This *should* have reduced copper:

|              |    |    |    |    |        |
|--------------|----|----|----|----|--------|
| Invert-sugar | .. | .. | .. | .. | 0.0311 |
| Levulose     | .. | .. | .. | .. | 0.0088 |

0.0399 Cu.

There were *found* Cu = 0.040.

3. Used: Same as Solution No. 1. This should have reduced copper, 0.2388 (based on 0.25 grammes dry substance).

There were found by proceeding as directed by Sieben, *i.e.*, by using 60 c.c. HCl of six times normal strength, and boiling for three hours 0.2934 Cu.

This proved that all the levulose was not destroyed, and indicated that either more acid must be used or that the solution would have to be boiled for a longer time. Both devices were tried, and both gave very satisfactory results.

Test 1.—Used: 120 c.c. HCl (6 × normal strength). Time of boiling, three hours. Copper reduced, 0.233.

Test 2.—Used: 60 c.c. HCl (6 × normal strength). Time of boiling, six hours. Copper reduced, 0.235.

To briefly resume, the foregoing data are here once more given in tabular form:

|  |    |    |    |    |                      |
|--|----|----|----|----|----------------------|
| Exp. 1.—Invert-sugar   | .. | .. | .. | .. | 0.09861              |
| Dextrose   | .. | .. | .. | .. | 0.15143              |
| Ratio of invert-sugar to dextrose, as 100: 154.                    |    |    |    |    |                      |
| Copper that should have been reduced                               | .. | .. | .. | .. | 0.3800               |
| Copper found   | .. | .. | .. | .. | 0.3826               |
| Exp. 2.—Invert-sugar   | .. | .. | .. | .. | 0.1628               |
| Levulose   | .. | .. | .. | .. | 0.1679               |
| Ratio of invert-sugar to levulose, as 100: 103.                    |    |    |    |    |                      |
| Copper that should have been reduced                               | .. | .. | .. | .. | 0.5860               |
| Copper found   | .. | .. | .. | .. | 0.5868               |
| Exp. 3.—Invert-sugar   | .. | .. | .. | .. | 0.273504             |
| Dextrose   | .. | .. | .. | .. | 0.0052096            |
| Ratio of invert-sugar to dextrose, as 100: 2.                      |    |    |    |    |                      |
| Copper that should have been reduced                               | .. | .. | .. | .. | 0.0095               |
| Copper found   | .. | .. | .. | .. | 0.0062               |
| Exp. 3a.—Invert-sugar  | .. | .. | .. | .. | 720810.0             |
| Dextrose   | .. | .. | .. | .. | .869986 <sup>0</sup> |
| Ratio of invert-sugar to dextrose, as 100: 4.5.                    |    |    |    |    |                      |
| Copper that should have been reduced                               | .. | .. | .. | .. | 0.02460              |
| Copper found   | .. | .. | .. | .. | 0.02185              |
| Exp. 4.—Invert-sugar   | .. | .. | .. | .. | 0.17908              |
| Levulose   | .. | .. | .. | .. | 0.0107415            |
| Ratio of invert-sugar to levulose, as 100: 6.                      |    |    |    |    |                      |
| Copper that should have been reduced                               | .. | .. | .. | .. | 0.2388               |
| Copper found after three hours' boiling                            | .. | .. | .. | .. | 0.2934               |
| Copper found after six hours' boiling                              | .. | .. | .. | .. | 0.235                |
| Copper found after three hours' boiling with double amount of acid | .. | .. | .. | .. | 0.233                |

As shown by these data, the proportion between the invert-sugar and the dextrose, or levulose, respectively, was made to vary between wide limits.

The work thus far given shows that this method devised for the determination of sucrose, invert-sugar, and dextrose or levulose, respectively, is perfectly feasible and practicable.

It, however, also discloses the fact that the directions given by Sieben for the destruction of the levulose—the process upon which this method of analysis depends wholly for its accuracy—do not meet *all* the possibilities. A careful investigation will therefore have to be made of the various conditions affecting the destruction of the levulose before judgment can be passed on the value of the method here under consideration.

Experiments to this end are now in progress, and the results obtained will be given in Part II. of this paper.

For valuable aid received in the execution of the analytical work here recorded, the writer wishes to express his obligations to his assistants, Messrs. Ziebolz and Brainerd.

### REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESS.

ESTIMATION OF IRON AND ALUMINA IN PHOSPHATES. R. JONES. (*Zeitschr. f. Angew. Chemie*, No. 1, '91).—The author having thoroughly tried Glaser's process (see ANALYST, 1890), thinks it may be improved by lessening the amount of sulphuric acid. The original process recommends 45 grammes of the strongest acid, but even if the sample solely consisted of calcic oxide, two grammes would be amply sufficient. As the measuring of strong sulphuric acid is troublesome, the author uses 10 c.c. of an acid which has been five times diluted. The author further thinks the quantity of phosphate used for analysis (4 grammes) is too small, at least one gramme should be used. The actual process is, then, as follows :—

10 grammes of the phosphate are dissolved in nitrohydrochloric acid, and the solution diluted up to 500 c.c. 50 c.c. (= 1 gramme) are evaporated to half the bulk, and while still hot, mixed with 10 c.c. of dilute sulphuric acid. 150 c.c. alcohol are next added, and the mixture allowed to settle for at least three hours. Glaser thought half an hour sufficient; but the author found this to be not long enough. The sulphate of lime is collected on a filter and washed with alcohol, the filtrate being collected in a Erlenmeyer's flask of half a litre capacity. The washing is finished when 10 drops of the washings, after dilution with an equal bulk of water, do not colour with methyl-orange. The filter and the precipitate is put into a platinum dish, the spirit is burned off, and the mass finally ignited and weighed.

The alcoholic solution is distilled off to recover the alcohol (which, however must be re-distilled over potash), and the residue rinsed into a beaker. Slight excess of ammonia is then added, and this again completely boiled off. This is very important, as it prevents the co-precipitation of magnesia.

The precipitate, consisting of ferric and alumina phosphates, is carefully collected on a filter, and washed four times with boiling water without disturbing it too much. If the washings should be turbid, washing with a very weak solution of neutral ammonium nitrate must be resorted to. The filtrate contains phosphoric acid, magnesia, besides, of course, sulphuric acid, and may be alkalies. The magnesium phosphate is

separated by addition of ammonia, and weighed; but the phosphoric acid and alkalis are best estimated in aliquot part of the original solution.

Many analysts prefer to remove the phosphoric acid by molybdate, and finally weigh the pure oxides. The author thinks this a very good plan, providing the phosphates of iron and alumina have been first isolated by Glaser's process before treating with molybdate. The phosphate must, however, be free from organic matter, otherwise a little of the alumina will escape precipitation.

L. DE K.

ESTIMATION OF NITROGEN IN PURE AND MIXED NITRATES. A. SULLWALD. (*Chem. Zeit.*, No. 99, 1890).—The author's process (really a modification of Jodlbauer's method) is as follows:—5 gram. of pure nitre, or 1 gram. of a mixture is put into a 150 c.c. flask and moistened with .5 c.c. of water. The addition of water serves to easier dissolve the substance, and also to prevent the mass from getting too hot; by means of a long funnel 20 c.c. sulphophenylic acid (20 grams. of phenol in 500 c.c. sulphuric acid) are slowly added. After thoroughly cooling 2.5 grams. of zinc-dust are added, and after a quarter of an hour some mercury is added, and the whole gradually heated to boiling. The ammonia is finally estimated as usual. If a sufficiently large and suitable flask is at disposal it is as well to distil off the ammonia from the same.

Although this process gives perfectly correct results, it is, according to the author, not quite so simple as the one proposed by O. Förster, which is as follows:—5 gram. of the nitrate is mixed with the usual precautions, with 15 c.c. of a 6 per cent. sulphuric acid solution of salicylic acid. When all is dissolved 5 grams. of hyposulphite of soda are added, and finally 10 c.c. of pure sulphuric acid and a little mercury.

L. DE K.

ASSAY OF COMMERCIAL ALUMINIUM. F. REGELSBERGER. (*Zeitch f. Angew Chemie* No. 1, 1891).—Klemp's process, based on the volume of hydrogen evolved when the metal is dissolved in potash-ley, is not correct, because all samples of commercial aluminium contain silicon, which also liberates hydrogen. For instance, a commercial sample containing 98 per cent. Al., and 1.5 per cent. Si., will give a volume of hydrogen corresponding with 99.9 per cent. of aluminium.

The author thinks it far better to carefully estimate the impurities in the metal, but if a direct estimation is required he proceeds as follows:—Two grams. of the sample are dissolved in a solution containing 15 grams. of pure caustic potash in a platinum vessel, and finally made up to 200 c.c. 50 c.c. (= .5 grm.) are now boiled with a slight excess of neutral ammonium nitrate, and the precipitated alumina collected and treated as usual. Allowance must of course be made for any alumina or silica the reagents may contain.

The alumina must be of course tested for silica.

L. DE K.

DISCLAIMER.—Mr. W. H. Stanger and Mr. Bertram Blount, of the Broadway Laboratory and Testing Works, Westminster, desire to correct a rumour which has become prevalent, by stating that the Mr. William Fox who is at present associated with them at the above address, is a member of the Institution of Civil Engineers, and not a practising analyst.

# THE ANALYST.

MARCH, 1891.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

An ordinary meeting was held at Burlington House on the 11th ult. The President, Mr. Hehner, in the chair.

The minutes of the annual meeting were read and confirmed.

On the ballot papers being opened Mr. Thomas Hughes, Public Analyst for Cardiff, was declared to be duly elected as a member.

The following gentlemen were proposed for election as members:—

Thomas Macfarlane, Chief Analyst to the Ottawa Laboratory; F. W. Babington, Assistant Analyst ditto; Edward Russell Budden, Consulting Technical Chemist; Thomas Hunter, Analytical Chemist, Bristol; W. L. Hiepe, Analytical Chemist, Manchester.

The following papers were read and discussed.

"On the Composition of Milk and Milk Products." By Dr. Vieth. "Remarks on the Analysis and Composition of Butter-Fat: a Criticism of recent Papers by Dr. Johnstone in the ANALYST and the *Chemical News*." By the President.

The next meeting of the Society will be held at Burlington House on Wednesday the 4th inst.

## A COMPARISON OF ENGLISH AND AMERICAN CIDER, WITH SUGGESTIONS FOR ESTIMATING THE AMOUNT OF ADDED WATER.

By GEORGE EMBREY.

(Read at Meeting, January, 1891.)

I HAVE no doubt the members of this Society are as well acquainted with the nature of as myself. In Gloucestershire the farmers use special varieties of the apple, and collect the crop in October. It is stacked in the orchard for three or four weeks, then

crushed in an extremely rude mill, the pulp allowed to remain several days and placed between cloths made of horse-hair; the juice is then allowed to ferment for three or four weeks, and finally placed in casks, from which it is drawn for bottling in the following April. A common method of fining is by adding one quart of milk to each eighteen gallons of cider. Salicylic acid is frequently used for preserving, in the proportion of one ounce to ninety-six gallons of the cider. At the end of three or four months that portion which has become sour is mixed with sugar and water, bottled, and sold as Herefordshire or Devonshire cider; never as Gloucestershire, the latter term being reserved for pure cider.

In some cases the following more scientific method is adopted. The fruit is bruised in a mill similar in structure to a root pulper, and is transferred to hair or manilla cloths, subjected first to hand pressure and afterwards removed to a hydraulic press, by which means the pips are crushed and the flavour of the product greatly improved. So completely is the juice removed that the remaining mass is air dried and used for fuel.

The juice is then allowed to stand until fermentation has just commenced, a period of twenty-four to thirty-six hours, and filtered through a layer, a foot thick, of decomposed granite, from which most of the clay has been removed by washing. The fermentation is then completed in the usual manner. Notwithstanding these precautions we are unable to produce a beverage equal to the Newtown Pippin cider brought over from America. The prejudice of Englishmen to American productions is now so great, especially in country districts, that, notwithstanding the superiority of the American products over our own, the statement is frequently made that Newtown Pippin cider is an artificial product and even chemists of some eminence have been unable to pronounce it pure. Some months since I was asked by a client to make such experiments as would help to clear up the matter, and the somewhat generous offer of £1,500 was made to me if I succeeded in proving the presence of anything besides fermented apple-juice. I am sorry to say that up to the present I have been unable to claim the prize, for in the interests of our local farmers I should be very glad to keep away the American supply.

I am rather astonished at the small amount of literature available in connection with the subject. Mr. Allen, in his valuable book on organic analysis, quotes the following analysis by R. Kayser.

|                          | Must.           | Cider.         |
|--------------------------|-----------------|----------------|
| Total Solid Matter .. .. | 16.25 per cent. | 2.36 per cent. |
| " " " yielding ash .. .. | .35 " "         | .31 " "        |
| Alcohol .. ..            | —               | 4.36 " "       |
| Malic Acid .. ..         | .33 " "         | .30 " "        |
| Acetic Acid .. ..        | —               | .08 " "        |
| Sugar .. ..              | 12.5 " "        | .75 " "        |

There is evidently some mistake here, as the total solid matter of cider is given as 2.36 per cent., probably 12.36 per cent. Then follows a table showing the mean of twenty analyses.

|                              | Average of twenty<br>Samples of Brittany<br>cider<br>(Rousseau). | Composition of<br>good ordinary<br>cider one year old<br>(Rabot). |
|------------------------------|--|---|
| Alcohol (by volume) .. ..    | 2.05 per cent.   | 5 to 6 per cent.  |
| Total Solid Matter .. ..     | 1.93 " "   | 3 " "   |
| " " " containing sugar .. .. | .25 " "  | —   |
| " " " " mineral matter .. .. | .15 " "  | .28 " "   |

These evidently relate to much watered ciders, for reasons which I shall give later.

Church gives the following as the composition of apples and pears, without stating the variety, the information being therefore of little value :—

|                         | Apples. |    |    |    | Pears. |    |    |    |
|-------------------------|---------|----|----|----|--------|----|----|----|
| Water .. ..             | 83.0    | .. | .. | .. | 84.0   | .. | .. | .. |
| Albumenoids, etc. .. .. | .4      | .. | .. | .. | .3     | .. | .. | .. |
| Sugar .. ..             | 6.8     | .. | .. | .. | 7.0    | .. | .. | .. |
| Malic acid .. ..        | 1.0     | .. | .. | .. | .1     | .. | .. | .. |
| Pectose and gum .. ..   | 5.2     | .. | .. | .. | 4.6    | .. | .. | .. |
| Cellulose .. ..         | 3.2     | .. | .. | .. | 3.7    | .. | .. | .. |
| Mineral Matter .. ..    | .4      | .. | .. | .. | .3     | .. | .. | .. |
|                         | 100.0   |    |    |    | 100.0  |    |    |    |

I am in a position to state that the difference in varieties of apples is so great as to account for the great difference in American and English ciders. The following five analyses will show the varieties to which I refer :—

|   | No. 1.  | No. 2.  | No. 3.  | No. 4. | No. 5.  |
|---|---------|---------|---------|--------|---------|
| Specific gravity .. ..                      | 1034.28 | 1033.48 | 1032.35 | 1010.0 | 1021.48 |
| Alcohol .. ..                               | 2.91    | 3.49    | 2.45    | 3.64   | 3.32    |
| Cane Sugar .. ..                            | —       | —       | —       | —      | —       |
| Grape sugar .. ..                           | 7.91    | 8.2     | 6.93    | .36    | 3.86    |
| Volatile acid calculated as acetic acid, .. | .096    | .048    | .128    | .222   | .144    |
| Fixed acid calculated as malic acid ..      | .33     | .671    | .712    | .244   | .244    |
| Ash .. ..                                   | .3      | .32     | .24     | .3     | .34     |
| Total extractive .. ..                      | 9.2     | 9.6     | 8.96    | 4.5    | 6.7     |

Nos. 1, 2, and 3 are American. No. 4 is an old English perry. No. 5 is a new English cider.

On comparing the three American ciders with the two samples of English, it will be seen that the extractive matter is greater in the former, and this is mainly due to the much larger quantity of fixed acid and sugar.

The following analysis shows the character of unfermented fruit juice from choice apples (table fruit) :—

|  |         |           |
|--|---------|-----------|
| Specific gravity .. ..                   | 1048.08 |           |
| Alcohol .. ..                            | .21     | per cent. |
| Sugar .. ..                              | 10.84   | " "       |
| Volatile acid calculated as acetic .. .. | .024    | " "       |
| Fixed .. .. malic                        | .549    | " "       |
| Ash .. ..                                | .3      | " "       |
| Total extractive .. ..                   | 12.06   | " "       |

I may mention that the malic acid and sugar increases with the quality of the fruit. I hope, on some future occasion, to submit to you a series of analyses showing the composition of the chief varieties of English apples.

Now, as regards the addition of water ; is it possible to discover this ?

The following is an analysis of prime Herefordshire bottled cider, made, as I have already indicated, from cider, water and sugar :—

|  | No. 6.  |           |
|--|---------|-----------|
| Specific gravity .. ..                   | 1023.08 |           |
| Alcohol .. ..                            | 2.22    | per cent. |
| Cane sugar .. ..                         | .85     | " "       |
| Grape sugar .. ..                        | 5.52    | " "       |
| Volatile acid calculated to acetic .. .. | .108    | " "       |
| Fixed .. .. malic                        | .22     | " "       |
| Ash .. ..                                | .16     | " "       |
| Total Extractive .. ..                   | 6.62    | " "       |



It will be seen that the amount of ash is only .16 per cent., and genuine cider not less than .25 to .35 per cent. I am inclined to fix these figures as the lowest and highest limits. Whenever the ash falls below .25 per cent., there is reason to believe that water has been added.

A short time since I asked a farmer to give me a sample of genuine cider, and on analysis it gave the following result:—

|  |                |
|--|----------------|
| Specific gravity .. .. .                   | 1014.68        |
| Alcohol .. .. .                            | 2.57 per cent. |
| Sugar .. .. .                              | 2.79 "         |
| Volatile acid calculated as acetic .. .. . | .192 "         |
| Fixed acid calculated as malic .. .. .     | .244 "         |
| Ash .. .. .                                | .2             |
| Total extractive.. .. .                    | 4.74           |

The ash here, .2 per cent., was lower than I expected, and asking him to try and recollect if any water had been added, he admitted that the mats had been washed with a few bucketsful which at once accounted for the reduction in amount of mineral matter. I can quite understand that it is possible for different amounts of ash to be yielded by products obtained from trees growing on a variety of soils, but I believe .25 is the lowest likely to be met with; again, ciders which have been watered, always contain added cane sugar, and almost always salicylic acid. On reference to analysis No. 6, it will be seen that the extractive matter consists mainly of sugar. I feel convinced that if the members in cider-producing districts will apply themselves to this question we shall soon be in a position to report added water in the case of cider with quite as much accuracy as in that of milk.

It is the low figure given for ash which leads me to believe that Mr. Allen's figure refers to watered samples.

#### DISCUSSION.

The PRESIDENT said they were all very grateful to Mr. Embrey for what he had done, which was very important, and a matter of great scientific interest. He should like to see a few more figures of ash.

Mr. EMBREY said these would be published.

Dr. TWEED asked Mr. Embrey if he had calculated the original gravity of the ciders, using Hofmann's tables for the original gravity of beer. If a falling-off was found both in original gravity and in ash, it would point to watering. If, on the other hand, the ash alone was deficient, and not the original gravity, it would point to watering and addition of saccharine material.

Dr. VIETH said he was afraid that the determination of the ash would be hardly sufficient to discover, and certainly not to ascertain the extent of an adulteration. The amount of ash present was very small, being .3 per cent. only, and distilled water was not likely to be used for adulteration.

Dr. MUTER asked if Mr. Embrey had tried taking the alkalinity of the ash at all? If something of that kind were done, the question of added water might be got over in that way. If Mr. Embrey had not tried it, it would be interesting for him to do so.

Mr. CASSAL said that the question of the definitions to be applied to articles of food had necessarily again been raised. He understood that Mr. Embrey would regard 0.25 per cent. of ash as characteristic of a genuine cider, and any departure from this figure as indicative of adulteration. This amounted to the creation of a definition. Mr. Embrey's figure was, no doubt, based upon a large number of determinations, but

it was hardly necessary to point out the great caution which ought to be exercised in accepting a limit of this kind for such a product as cider. As public analysts they would have to come to a decision in this as in other matters, and, while admitting the great value of Mr. Embrey's work, it would be very desirable to have something more to go upon. Determination of original gravity, as had been suggested, and of the degree of alkalinity of the ash, might afford valuable supplementary information. There ought to be no difficulty in the way of prosecuting for admixture of salicylic acid with cider, even supposing that the salicylic acid used was absolutely pure, which they very well knew was not the case. He remembered seeing some cider presses on the continent several years ago partly coated with lead. Had Mr. Embrey come across anything of the kind, and had he examined cider for poisonous metals?

Mr. COSTE inquired whether Mr. Embrey had examined both draught and bottled cider, since there was sometimes a very great difference in flavour between these. It was popularly supposed that hops were often added to the latter, the taste of which in some cases resembled that of ale rather than draught cider.

Mr. EMBREY, in reply, said his experience was confined entirely to Gloucestershire. There was certainly a vast difference between bottled and draught cider, and so much importance was attached to some bottled cider that it fetched as much as 48s. a dozen. He had never seen lead used, but iron was common enough for bolts and so on, and he had never found any other poisonous metals in cider. He had never calculated the original gravity in the way indicated, but would try and do so, although he had his doubts as to whether it could be done. As regards the ash, he always searched for mineral acids. On ignition, if the soluble ash was alkaline, they might be sure there was no sulphuric acid. Gloucestershire well waters contained from 50 to 60 per 100,000 of mineral water. The reason he brought the paper before them was that the inspectors in his district proposed buying samples of cider, and he thought it would be desirable to have the views of the Society.

## REMARKS ON THE ANALYSIS AND COMPOSITION OF BUTTER-FAT— A CRITICISM.

By OTTO HEHNER.

(Read at Meeting, February, 1891.)

IN the February number of the ANALYST (Vol. XVI.) and in the *Chemical News* of January 31st (Vol. LXIII.) are contained two papers by Mr. W. Johnstone on the Composition of Butter-fat, containing statements and views, so startling that they will probably have received some attention from public analysts.

As the paper in the ANALYST is the more explicit, and embraces most of the statements contained in the article in the *Chemical News*, I propose to lay before you a criticism mainly of the former paper.

It will be seen that the paper is divided into two sections, one devoted to analytical results, the other to theories based upon these.

The principle of working, as adopted by Mr. Johnstone, is simple and old. He ascertains, as a number of chemists have proposed before him, the total amount of alkali necessary to saponify a weighed quantity of butter. He then separates, washes, dries, and weighs the insoluble fatty acids, and finally dissolves these and titrates the acidity, the difference between the two titrations being calculated into butyric acid.

The method is therefore a combination of Koettstorfer's principle and that introduced by myself, and sound when properly carried out.

The means of saponification adopted will appear clumsy to those accustomed to butter analysis, and objection will probably be raised to the use of aqueous normal alkali, as almost certain to cause introduction of carbonates, which are well known to be fatal to accurate work when phenolphthalein is used as an indicator. No special precautions as to this head are mentioned in the paper, and it would be fair to the author to assume that such precautions were not neglected, did not the tabulated results raise doubts in the mind of the critic, as will be seen in the following :

The Koettstorfer process has been used upon thousands of samples of butter and of other fats since it was first published, and it will be held to be established beyond possibility of doubt that, whilst butter-fat uses from 22.15 to 23.27 per cent. of KHO for saponification (Allen, ANALYST Vol. XI., p 145), corresponding to a saponification equivalent from 241 to 253, animal fats of the beef-fat class use only from 19.2 to 19.8 per cent. of KHO, corresponding to an equivalent of 283 to 292.

Mr. Johnstone's statements as to the potash neutralising power of butter-fat and of beef-fat are utterly at variance with the above. He finds two butters, 2.5 gram. of which use 11.50 and 11.92 c.c. of normal alkali for saponification, equal to 25.8 and 26.75 per cent. of KHO, or an equivalent of 217.11 and 209.7 respectively, whilst his sample of beef-fat uses 23.69 per cent. of alkali, equivalent 236.8.

Now, whatever the composition of butter may be, it is proved beyond dispute that beef-fat consists almost wholly of stearine, palmitin, and oleine, with saponification equivalents of 296.7, 268.7, and 294.7.

Simple as is the Koettstorfer process, it does not involve, when worked by a skilled operator, any sources of error which should lead to differences such as I have pointed out.

It is then attempted to be shown in the paper that when the titration of the excess of alkali is carried out at a temperature of between 80° to 95°F. lower results are obtained than at 60°F., at the latter temperature the proportion of KHO consumed rising from 25.6 to 27.78 and from 26.75 to 27.71 per cent. respectively.

I recall the mode of procedure adopted by Mr. Johnstone :—To 2.5 grams. fat, 2 oz. of 95 per cent. alcohol, 1 oz. ether, and 25 c.c. aqueous normal soda solution are added, and after saponification, another 3 oz. of proof spirit. We have thus a solution containing about 64 per cent. of alcohol and ether and about 36 per cent. of water as solvents.

Should the aqueous normal soda have contained sodium carbonate, this would in the cold partially separate from this solution, reducing its alkalinity, the precipitated sodium carbonate being counted as alkali used for saponification. On reheating this sodium carbonate would dissolve and consume a further quantity of normal acid, as stated by the author.

The saponification equivalents of the insoluble fatty acids which may readily be calculated from the weights given on page 28, and the volumes of normal soda consumed, are equally extraordinary. Thus the fatty acids from butter I. had an equivalent of 260.9, of II. 251.0, and from beef-fat of 223.8. Now it is well known that the equivalent of insoluble butter acids is somewhat smaller than that of fatty acids from

beef, instead of far larger, as given by our author. The fatty acids from beef have an equivalent lying between that of palmitic (266) and stearic and oleic (282 and 284), whilst Mr. Johnstone finds only 223·8!

It is impossible to avoid coming to the conclusion that the results published by Mr. Johnstone in the ANALYST are not deserving of confidence, as far as the saponification experiments are concerned.

From these extraordinary results the percentage of butyric acid is calculated by the author under review. The results, as might be expected, are again incompatible with ascertained facts. 11·7 per cent. of butyric acid are thus deduced to be present, or almost 50 per cent. more than the most careful experiments have shown to be contained in butter-fat. Curiously enough, this figure is corroborated by a direct distillation experiment, recorded on page 32. Here again I refrain from attempting any explanation, but let analysts draw their own conclusions.

Upon this substructure of analyses Mr. Johnstone proceeds to build up his theories. According to him there are two kinds of butter-fat. The first and simpler kind (which I will call A), consists of one homogenous molecule, in which iso-oleic, palmitic, and capric acid are held together by a glycerine molecule; whilst in the second kind another molecule (B), consisting of the fatty acid  $C_{19}$ , and heptylic acid, held together by glycerine, is mixed in various proportions with the iso-oleic molecule.

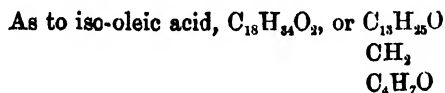
Concerning the molecule No. A, on saponification it should yield, besides glycerine, palmitic, capric acid, and iso-oleic acid, which latter splits up by treatment with sodium hydrate into tridecylic acid ( $C_{13}H_{26}O_2$ ), butyric acid, methyl-alcohol, and hydrogen.

Concerning the latter, the formula requires that 2·5 grams. of butter-fat furnish no less than 74·5 c.c. of hydrogen, an interesting and certainly very novel discovery if it would but fit in with the facts. It is well known that if alkali free from carbonic acid be used for saponification no trace of gas is evolved during or after saponification, let alone 74·5 cubic centimetres of hydrogen.

The author certainly speaks of the evolution of a continuous stream of small bubbles during one period of his operations, and he probably bases upon that circumstance the assumption that hydrogen is evolved; but unfortunately his continuous stream of bubbles evolves, not *during* the saponification, as the formula requires, but *after* the saponification is completed and after the free alkali has been neutralised with normal acid, the bubbles undoubtedly being carbonic acid, from the standard alkali solution.

Molecule A weighs 748, and requires four equivalents of KHO for resolution, or exactly 30 per cent., instead of 22 to 23 actually used by butter-fat, or instead of 25·8 and 26·7 found by Mr. Johnstone himself on the very butters which he declares to consist of this interesting compound.

The three insoluble fatty acids from molecule A have a total calculated equivalent of 642, hence an average equivalent of 214, against 260·9 and 251·0 observed by Mr. Johnstone.



Chemists might have a right to expect some evidence of its existence, were it ever so slight. No fatty acid, primary or secondary, is at present known, which by heating with alcoholic or aqueous potash solution resolves itself into two acids of lower atomic weight and marsh gas, or methylic alcohol and hydrogen.

Against the allegation that certain butters at least consist of a homogenous molecular compound, we have the indisputable fact, first pointed out by Dr. J. Bell, and lately again by Cochran (*ANALYST*, Vol. XIII., p 55), that by treatment with alcohol every sample hitherto examined furnishes oily matter with a larger proportion of volatile acids and a less proportion of insoluble acids than was present in the entire sample; also that by pressure, or by fusion and partial crystallisation, a similar separation is observed, a circumstance utterly incompatible with the theory that butter-fat is a uniform compound.

On the other hand, if it were possible to dissolve molecule A in alcohol, there would exist certain butters, which must be entirely soluble in alcohol; others from which from 50 to 60 per cent., containing the whole of the volatile acid, could be extracted, leaving a residue free from butyric acid. This, I need not point out, is not borne out by experience.

Turning our attention to molecule B we meet with the statement that this furnishes on saponification; two molecules of  $C_{19}H_{38}O_2$  (an acid hitherto unknown), and heptylic acid. The average equivalent of these is 242, that is to say, also lower than the total equivalent found by Mr. Johnstone of insoluble butter acids. I would here point out that heptylic acid is not quite insoluble in water as assumed by the author in constructing his formula.

Here again we fail to find a particle of evidence in support of the formula. Yet we are told that if the analyst be fortunate enough to detect stearic acid in a sample of butter, he need have no hesitation in declaring it adulterated. But it does not seem to strike the writer in question that a most delicate analysis would be required to distinguish the  $C_{19}$  acid from stearic, the former using 18.83 per cent of KHO for saponification, the latter 19.75 per cent.

The samples of butter previously commented upon were of an abnormal nature, the percentage of insoluble fatty acids furnished by them being extraordinarily low. The author, therefore, furnishes us also with the analysis of three samples, A, W, and Y, in which the fatty acids are equally extraordinarily high. Indeed normal samples do not seem to have been examined by the author in question. Calculating from their stated composition the percentages of KHO required for saponification, we find for A 27.00 per cent., for W 26.35, and Y 27.22 per cent., figures which are utterly at variance with every-day experience.

The whole of the fatty acids stated by Mr. Johnstone to exist in butter-fat are saturated fatty acids. As, however, butter-fat and the fatty acid from butter has a considerable iodine absorption, about 31 per cent. (corresponding to about 36 per cent. of oleic acid), whilst saturated fatty acids are incapable of absorbing iodine, the theory further clashes with the facts. And further, we know, from the circumstances that butter-fat has an acetylation figure of some magnitude, that it must contain a large proportion of hydroxy-acids. For these also the discoverer has no room in the formulae given by him.

The observation that the solid fatty acid which collects in the condenser consists mainly of capric acid had been made long before Mr. Johnstone took up the subject.

It might well be held that such a paper needed no criticism and refutation. And indeed it is melancholy work to criticise it. It would, however, tend to discredit English chemistry were it believed that such a research as that published by Mr. Johnstone passed unchallenged or met with the approval of anyone conversant with the subject.

Much remains to be done before the actual constitution of butter-fat is explained; the pages of many volumes of our journal, and of chemical literature generally, prove it; but theories without proof, juggling with formulæ without regard for facts, will never bring us nearer to the solution of this problem. Meanwhile, this problem should not be confounded, as it is by the author whom I have been criticising, with the question of butter *analysis*. In the *Chemical News* of January 30th, Mr. Johnstone places "butter analysis on a satisfactory basis." In the ANALYST of February 1st, butter analysis is declared by him to be "in a most unsatisfactory state at present." Very unsatisfactory indeed is the proof of some of the assertions referred to, but the subject of *butter analysis* is left untouched by the author.

Since working at the above paper I am informed that Mr. W. Johnstone has notified his withdrawal of the whole of the theoretical part of his paper in THE ANALYST. As his assertions have gone out to the world I see no reason to keep back my criticisms\* on either his alleged statements or his theories.

But I may be allowed to quote from his letter of withdrawal the following reasons: "I ventured to suggest such a theory on two determinations, namely, on that of the soluble fatty acids calculated as butyric acid, and on the amount of glycerine, calculated from the amount of oxalic acid formed on boiling with alkaline permanganate."

"My reason for withdrawing that theory is that since the writing of that paper I find that butyric acid is easily converted into oxalic acid by boiling with alkaline permanganate, thus:  $C_4H_7O_2 = 2C_2H_2O_4 + H_2$ . The following quantities of butyric acid were taken and boiled with alkaline permanganate and the oxalic acid resulting from same estimated and calculated into butyric acid.

|                            |       |       |
|----------------------------|-------|-------|
| Butyric acid taken .. .. . | ·3916 | ·1858 |
| „ „ found .. .. .          | ·3684 | ·1740 |

I have also tried the bichromate process, and have found no difficulty in readily oxidising the butyric acid into carbonic acid. So much, therefore, for trusting to processes advanced by Messrs. Allen and Gehlen without verifying their accuracy."

In the first place, it will be seen that if butyric acid were really oxidised into oxalic acid in the manner described, the experimenter should have obtained a figure far higher than the theoretical one, whilst precisely the contrary is the case. He *calculates* glyceryl 5·82 and 6·03 (by the way, here glyceryl means  $C_3H_7$ , not the usually accepted radical  $C_3H_5$ ), and *finds* 5·01 and 5·04. In the second place, butyric acid *does not yield a trace even of oxalic acid with alkaline permanganate*, as I have proved to my satisfaction, *much less does it yield a quantitative amount*. Here one cannot even conjecture how Mr. Johnstone obtains his results. It certainly seems somewhat peculiar to see quantitative results given as to the oxalic acid produced, when it is a well-known

fact that alkaline permanganate oxidises butyric acid into *carbonic acid*. (See Beilstein, Org. Chem., Vol. I., p 402). In the third place, as to the bichromate process, I have stated in my papers on the subject that I had tried the action of bichromate on butyric acid under the conditions of the process published by me, and found that it was not attacked. On the other hand, I was and am well aware that butyric acid treated with *concentrated* sulphuric acid and chromic acid is oxidised into  $\text{CO}_2$  and acetic acid. I have now repeated the trial. To about 100c. of distilled water about 25 c. of strong sulphuric acid were added, and some pure butyric acid. To the hot mixture a small drop of bichromate solution was added, not the faintest reduction being observed, even after some hours' heating.

I fear, therefore, Mr. Johnston's retraction wants a further withdrawal.

#### DISCUSSION.

Dr. DUFRE (who had taken the chair as senior Vice-President) said—Gentlemen, allow me in the first place to express my great pleasure at seeing Mr. Hehner in the chair of our society. I am quite sure that no one has worked harder and better for the success of the society, and there is no doubt we have attained success—a success in great measure due to the admirable work of Mr. Hehner. I take this first opportunity of stating this because, unfortunately, I was unable to be present when he was elected, or I would have given my vote for him with more pleasure than I have ever given a vote before. As regards this paper, there are a number of analysts here who have considerable experience on the subject, and you will probably like to hear them.

Mr. ALLEN said that his name having been mentioned in the letter of withdrawal from Dr. Johnstone, read by Mr. Hehner, he desired to say a few words on the subject in question. Dr. Johnstone alleged that he (Mr. Allen) had stated that no oxalic acid was formed by the oxidation of butyric acid by permanganate in alkaline solution, which is in opposition to Dr. Johnstone's experience, described in his letter withdrawing his theory of the constitution of butter. But he (Mr. Allen) was unaware that he had ever made the statement ascribed to him by Dr. Johnstone, and dismissed somewhat contemptuously by him. Dr. Johnstone must be aware of his (Mr. Allen's) exact position in the matter, for only a few days previously he (Mr. Allen) had furnished him, by request, with the references to the *Journal of the Society of Chemical Industry and Commercial Organic Analysis*, in which particulars of the process of estimating glycerine by conversion into oxalic acid with permanganate in alkaline solution were given. On page 292 of Vol. II. of the latter work the following passage occurred:—"The writer (Mr. Allen) has proved by experiments on known quantities of oxalic acid that that body is not acted on by permanganate in strongly alkaline solution, and *Benedikt and Zeigmondy* have found that the soluble fatty acids of oils, such as acetic, butyric, caproic, etc., do not, by treatment with the same reagent, yield any acids the calcium salts of which are precipitated from acetic solutions. The higher fatty acids of the stearic series are insoluble in water, and hence would not in any case interfere. On the other hand, certain acids of the acrylic or oleic series, and possibly oleic acid itself, yield oxalic acid by oxidation with permanganate. The higher acids of the oleic series are, however, insoluble in water, and the lower are not known to occur in fixed oils under normal conditions. Under certain circumstances, however, the method is wholly invalidated." With this passage presumably before him it was strange that Dr. Johnstone should assert that he (Mr. Allen) had found butyric acid to yield no oxalic acid by oxidation with alkaline permanganate. Not, however, that he thought much weight should be attached to Dr. Johnstone's statement that oxalic acid was formed. It was just possible that Dr. Johnstone had not worked on normal butyric acid at all, and it was barely possible that if he used

isobutyric acid he might get oxalic acid by its oxidation, though even this was opposed to the experience of other observers, who found that iso-hydroxy butyric acid was formed, the calcium salt of which was very soluble, and could not be mistaken for calcium oxalate. Dr. Johnstone's observation, therefore, required confirmation before it could be accepted as accurate. With regard to formation of carbonic acid from butyric acid by oxidation with chromic acid in acid solution, it was quite possible that such a result might be obtained if Dr. Johnstone employed a very hot and concentrated oxidising mixture. But with the ordinary chromic acid mixture his experience was completely opposed to that of other observers, and to what was to be expected from analogy. Thus E. T. Chapman, with whom the process originated, found acetic, propionic, and valeric acids to suffer no change by treatment with chromic acid mixture of moderate strength. Further, the modification of amylic alcohol having the constitution of a methyl-propyl-carbinol yielded the theoretical quantity of butyric acid with chromic acid mixture, and this underwent no further change. At a later date Chapman and Thorpe actually employed butyrate of ethyl as a body simply yielding acetic and butyric acids on oxidation, and obtained results which conclusively showed that the butyric acid was perfectly stable under the conditions of the experiment. Under these circumstances there was probably some fallacy underlying Dr. Johnstone's experiences, and this was the more likely as he had made public in the communications just criticised by the President a number of figures which on the face of them were absolutely inconsistent with probability, if not with possibility. He thought Mr. Hehner had done right in calling the attention of chemists to the nature of the experimental evidence on which Dr. Johnstone had founded his remarkable theories. It was extremely difficult to understand how Dr. Johnstone could have obtained such astonishing results, and still more surprising that he had not perceived the true interpretation of them.

Mr. CASSAL said that, had it not been for the necessity of repudiating this production on behalf of the Society of Public Analysts, it might be thought that it had been dealt with sufficiently. It was exceedingly unfortunate that the necessity had arisen, but the fact that the "paper" had appeared in the pages of THE ANALYST left them no alternative. In examining this curious paper, the main difficulty—after having unravelled the knotted language in which it was couched—was to make out what the author meant to convey. It would appear that he intended to give to the world some fragments of a transcendental chemistry known to himself alone, and the existence of which had not previously been even suspected.

(The letter of withdrawal from Dr. Johnstone, referred to in Mr. Hehner's paper and in the discussion that follows it, was addressed to the Editor of the ANALYST, who deemed it right, in consequence of certain of its contents, to communicate it to Mr. Hehner, since he (Mr. Hehner) had already given notice of his criticism of Dr. Johnstone's already published paper. Since the meeting at which Mr. Hehner's communication was read and discussed, Dr. Johnstone has written to the Editor requesting that his letter of withdrawal should not be published, and accordingly it does not appear, though its purport is conveyed in the extracts given above.)

*(Conclusion of the Society's Proceedings.)*

## VOLUMETRIC ESTIMATION OF GASEOUS OXYGEN BY MEANS OF NITRIC OXIDE.\*

By Prof. Dr. L. L. DE KONINCK (and Mr. ENNOT, *Pharmacist*).

WHEN a few months ago I made experiments on the volumetric estimation of free oxygen by means of metallic solutions, chiefly with an alkaline solution of ferrous

\* *Zeitsch. F. Angew. Chemie*, Feb. 1891.



tartrate, I also made some experiments concerning the original process of Priestly, which has been classed by W. Winkler among the abandoned methods.

The results were, just as might have been expected from previous experiments conducted by Berthelot and Lunge, very irregular and unsatisfactory. My work confirmed the results of Winkler, who previously had made experiments on the estimation of nitric oxide by means of air or oxygen, and who remarks:—"The contraction multiplied by two-thirds ought to have corresponded with the original nitric oxide, but was in effect a varying quantity."

A short time ago my attention was again called to this question by two articles from Messrs. Wanklyn and Cooper. In their first notice they not only called the nitric oxide process an accurate one, but even the best method ever known. In their second notice they communicated a very few test analyses to show the accuracy of the process:—

| A.                |       | 1.          | 2.            |
|-------------------|-------|-------------|---------------|
| Pure oxygen taken | ..    | 30 c.c.     | 40 c.c.       |
| " " found         | ..    | 30·6 c.c.   | 39·27 c.c.    |
| Error             | .. .. | 2 per cent. | 1·8 per cent. |

I abstain from any comments.

| B.                 |    | 1.            | 2.            | 3.            |
|--------------------|----|---------------|---------------|---------------|
| Air taken          | .. | 80 c.c.       | 50 c.c.       | 70 c.c.       |
| Oxygen found       | .. | 16·47 c.c.    | 10·27 c.c.    | 14·47 c.c.    |
| Experimental error | .. | ·33 per cent. | ·38 per cent. | ·25 per cent. |

Assuming air to contain 20·92 per cent. of oxygen, the errors in these experiments are comparatively small.

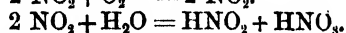
In consequence of these publications, I thought it best to repeat some of my experiments before replying to these authors, particularly as I had not kept any record of the figures of my previous work.

The *modus operandi* which I have followed is practically identical with that of Messrs. Wanklyn and Cooper—at least as far as I can judge from their extremely brief notices. If there should be any difference, it will be perhaps the preparation of the nitric oxide. The experiments were conducted in the following manner:—

An old-fashioned Hempel's hydrogen pipette, containing a spiral of sheet copper, is filled with dilute nitric acid of 1·1 spec. gravity. In the same way as hydrogen is prepared by means of zinc and sulphuric acid, nitric oxide is formed when required, although very slowly, and the apparatus always contains a certain quantity of the gas. But even with this dilute acid the gas is not perfectly colourless, but a faint yellowish tinge betrays the presence of traces of nitric peroxide. To prevent any analytical errors, the gas was in every experiment treated with water before measuring. In carrying out an analysis the oxygen (or air) and the nitric oxide must be, of course, measured separately, and afterwards mixed over water. On account of its simplicity and easy execution, I have preferred the following plan:—The gas (air) is introduced into a Winkler-Hempel burette; the nitric oxide is introduced into a similar apparatus, and, as already mentioned, well shaken with the water to remove any peroxide, and also to saturate the water with the oxide. After a few minutes' rest the volume of the two

gases are recorded, and after connecting the two burettes with a capillary tube filled with water, the oxygen is forced into the nitric oxide, and the two burettes are now disconnected. After thoroughly shaking the burette to assist the absorption, the volume of the gas is read off with the usual precautions. It is as well to wait for about twelve or fifteen minutes, so as to get the temperature, and consequently the volume constant. As the residue contains nitric oxide, the experiment must be conducted as described, viz., the oxygen must be mixed with the nitric oxide. If the nitric oxide were forced into the oxygen, it would amount to measure a mixture of the two gases in the same burette, and as both are slightly soluble in water, errors would be introduced.

The calculated figures in the table have been got by assuming air to contain 20·92 per cent. of oxygen, and the process to proceed according to the equation :



The contraction, according to these formulæ is equal to three times the amount of oxygen.

#### A. ATMOSPHERIC AIR.

| No. | C.C.'s of air. | C.C.'s of added NO. | Sum. | Residue left. | Contraction. | Oxygen calculated. | Experimental error. | Ratio between contraction and oxygen. |
|-----|----------------|---------------------|------|---------------|--------------|--------------------|---------------------|---------------------------------------|
| 1   | 50             | 45·1                | 95·1 | 62·4          | 32·7         | 21·80              | +·88                | 1—3·13                                |
| 2   | 49·6           | 40·7                | 90·3 | 52·2          | 33·1         | 25·60              | +4·68               | 1—3·67                                |
| 3   | 49·3           | 40·6                | 90·4 | 54·0          | 36·4         | 24·37              | +3·45               | 1—3·49                                |
| 4   | 50·0           | 37·0                | 87·0 | 52·8          | 34·2         | 22·80              | +1·88               | 1—3·27                                |
| 5   | 50·0           | 36·6                | 86·6 | 52·6          | 34·0         | 22·67              | +1·75               | 1—3·25                                |
| 6   | 50·0           | 36·6                | 86·6 | 52·6          | 34·0         | 22·67              | +1·75               | 1—3·25                                |
| 7   | 50·0           | 34·8                | 84·8 | 51·2          | 33·6         | 22·40              | +1·48               | 1—3·21                                |
| 8   | 50·0           | 29·5                | 79·5 | 45·8          | 33·7         | 22·47              | +1·55               | 1—3·22                                |
| 9   | 50·0           | 28·8                | 78·8 | 45·7          | 33·1         | 22·07              | +1·15               | 1—3·16                                |
| 10  | 50·0           | 24·4                | 74·4 | 44·0          | 30·4         | 20·27              | —·65                | 1—2·91                                |
| 11  | 50·0           | 21·0                | 71·0 | 45·6          | 25·4         | 16·93              | —3·99               | 1—2·43                                |
| 12  | 50·0           | 21·0                | 71·0 | 45·6          | 25·4         | 16·93              | —3·99               | 1—2·43                                |
| 13  | 50·0           | 20·9                | 70·9 | 45·6          | 24·3         | 16·20              | —4·72               | 1—2·32                                |

#### B. MIXTURE OF OXYGEN AND NITROGEN CONTAINING 17·6 N.

|    |      |      |      |      |      |       |       |        |
|----|------|------|------|------|------|-------|-------|--------|
| 14 | 49·2 | 41·4 | 90·6 | 58·0 | 32·6 | 22·09 | +4·49 | 1—3·76 |
| 15 | 51·1 | 51·1 | 93·2 | 64·0 | 29·2 | 19·04 | +1·14 | 1—3·25 |
| 16 | 50·0 | 50·0 | 80·2 | 55·1 | 25·1 | 16·73 | —·87  | 1—2·85 |

#### C. PURE OXYGEN.

|    |      |      |      |      |      |       |       |        |
|----|------|------|------|------|------|-------|-------|--------|
| 17 | 16·5 | 80·4 | 96·9 | 48·6 | 48·3 | 97·58 | —2·42 | 1—2·85 |
|----|------|------|------|------|------|-------|-------|--------|

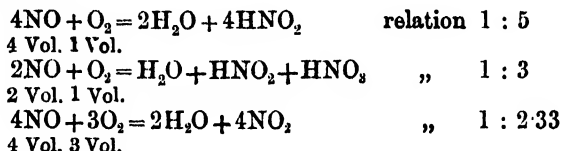
#### D. USE OF NITRIC OXIDE MIXED WITH NITROGEN.

Experiment No. 18. To the residual gas of No. 7 62·4 c.c., which, as may be easily calculated consisted of 39·4 c.c. nitrogen and 22·86 of nitric oxide, 20 c.c. of air was added, and then 15·82 c.c. of nitrogen and 4·18 of oxygen—total, therefore, 82·4 c.c. After the reaction was over, the residue measured 68·2 c.c., which equals a contraction of 14·2 c.c., and the relation between this and the oxygen as 3·40 : 1.

From an analytical point of view, these figures need no comment ; a process which gives results varying from 77·5—122·5 instead of 100 is absolutely useless.

From a general point of view, the comparison of the different experiments gives rise to some observations which are not without interest.

The relation between the volume of the oxygen and the contraction after the action of the nitric oxide, may theoretically vary between 1 : 2·33 and 1 : 5, as the following equations will make clear :—



The experiments Nos. 2-13 show that when the amount of nitric oxide increases this causes a larger proportion of nitrous acid to form, if the mixing of the gases is done under the same conditions. In experiment No. 2, three-fourths of the nitric oxide had been converted into nitrous acid, as is proved by the corresponding formulae :



In experiment No. 13, we see, on the other hand, the complete conversion of the nitric oxide into nitric acid, although, from the amount of nitric oxide used, we might have expected it to yield equal parts of nitrous and nitric acids. The comparison of experiments 1 and 2, also of Nos. 14 and 15, shows the influence on the result of the celerity with which the gases have been mixed and shaken with the water (Nos. 1 and 15 were very rapidly mixed). Finally, No. 18 shows that the dilution of the oxygen and nitric oxide mixture with an inert gas, which of course retards the reaction, favours the formation of nitrous acid.

## METHODS IN USE AT THE LABORATORY OF THE BOURSE DE COMMERCE, PARIS.

By M. FERDINAND JEAN, DIRECTOR OF THE LABORATORY.

### I.—EXAMINATION OF WAX FOR ADULTERATIONS.

#### (1.) ESTIMATION OF STEARIC ACID.

INTRODUCE into a flask 3 or 4 grams. of the sample for analysis, and bring it to the boiling point with 60 c.c. of alcohol of 96° ; shake whilst cooling, and then titrate the alcoholic solution with half normal soda, employing phenol phthalein as an indicator. Wax being only slightly soluble in cold alcohol, there is no need to take notice of its acidity, and the amount of the mixture can be calculated as stearic acid from the number of c.c. normal soda used in the titration, knowing that 7·8 c.c. of half normal soda = 1 gram. of commercial stearic acid.

#### (2.) ESTIMATION OF PARAFFIN AND OF MYRISTIC ACID.

To the flask containing the neutralised alcoholic solution, add 3 to 4 c.c. of solution of soda of 50 per cent. ; attach the flask to an upright condenser and heat for an hour to saponify. The saponification being complete, distil off the excess of alcohol, put the residue into a capsule, mix with dry sand and short asbestos, dry at 100°, pulverise and

extract it with warm chloroform (or petroleum ether), which dissolves the whole of the paraffin and the myristic acid, representing a part of the wax. To separate the paraffin, Horn has recommended acetalisation and solution of the produced ether by means of acetic acid, in which paraffin is insoluble. According to Horn, saponified wax should, under these conditions, yield 50 per cent. of matters soluble in glacial acetic acid. Following Horn's process, we have neither been able to properly separate the paraffin nor to obtain a constant factor for the part of the wax soluble in chloroform.

We effect this separation in the following manner :—

The chloroform holding in solution a part of the wax and all the paraffin is distilled off in a weighed flask, and the residue, having been dried at 100, is weighed.

Then weigh, in a small flask, a part of the residue left by the evaporation of the chloroform, and treat it under an upright condenser for an hour with 4 to 5 c.c. of anhydrous acetic acid. The acetalisation being complete, pour the resulting fluid into a glass tube graduated in 10 c.c. and divided into tenths; rinse the flask with boiling crystallisable acetic acid, and turn the whole into the graduated tube. The volume of the liquid should be about 9 c.c. Place the tube in a water-bath at 90°, then close it up with a cork and shake it forcibly so as to well emulsify the liquids, and replace in the water-bath.

When the acetic acid has become clear, the volume of insoluble matter which floats on the acid is read off. Renew the shaking and place in the water-bath until a constant volume of paraffin insoluble in acetic acid is obtained, of which calculate the weight, remembering that 1 gram. of paraffin — from 1.35 to 1.4 c.c. On deducting the weight of the paraffin from the weight of the residue furnished by the chloroform, we obtain by difference the weight of the portion of the saponified wax soluble in chloroform.

### (3.) ESTIMATION OF STEARIN.

The saponified part insoluble in chloroform is formed by the soap of stearic acid and of stearin and by saponified cerotic acid. To estimate the stearin, dissolve in boiling water, filter to separate the sand and asbestos, and decompose the filtered liquor by a slight excess of nitric acid diluted so as to set free the fatty acids, filter and estimate the glycerine in the filtered liquid (after neutralisation and precipitation by plumbic acetate), by the potassium bichromate process. From the weight of the glycerine, calculate the stearin or suet, keeping in mind that 5 of anhydrous glycerine = 95 of stearin.

In cases where the proportion of stearin is small, it would be preferable to saponify 10 or 25 grams. of the substance and to estimate the glycerine by the bichromate process.

We therefore estimate by this method :—

1. Stearic acid by alkalimetry.
2. Paraffin by measuring the part insoluble in acetic acid.
3. A part of the wax (myristic acid) by deducting the paraffin residue from the weight of the residue soluble in chloroform.
4. Stearin by the estimation of glycerine.
5. The second part of the wax (cerotic acid) by difference.

## II.—ANALYSIS OF WINE.

## (1) ESTIMATION OF GLYCEBINE.

Evaporate 250 c.c. of the wine to the volume of 100 c.c., then agitate this concentrated liquid with freshly precipitated plumbic oxide, and render it slightly alkaline with baryta water. Filter, wash, and neutralise the filtrate with dilute sulphuric acid. Concentrate in a flat porcelain capsule, and when the volume of the liquid has been reduced to 50 c.c. incorporate therein 5 grams. of plumbic oxide, 10 grams. of sand, and 20 grams. of barium sulphate, evaporate and dry at  $100^{\circ}$  C. During this drying the basin should be covered with a plate of glass to avoid spurting. The dried mass, having been powdered, is extracted with a mixture of equal parts of alcohol and ether, the extraction being continued until 60 c.c. of liquid has been obtained. Thirty cubic centimeters of this liquid is placed in a tared glass capsule, and 20 grams. of dried and powdered litharge having been added, the whole is evaporated in the water-bath, and then dried to a constant weight between  $105$  and  $106^{\circ}$  C. The other 30 c.c. is evaporated in a tared glass capsule 6 centimeters in diameter, and the residue is placed in the air bath between  $160$  and  $170^{\circ}$  C. until a constant weight is obtained.

The weight of residue No. 1, after deducting that of the litharge and capsule employed, *minus* the weight of residue No. 2, being first multiplied by 1.243, and then by 8, gives the weight of glycerine present in a litre of the wine.

## (2) ESTIMATION OF ASTRINGENT ACIDS.

(a) *Estimation of Oenontannin.*

Concentrate 200 c.c. of wine down to 100 c.c., shake with an excess of freshly precipitated arsenious sulphide, filter and wash. Concentrate the filtrate to 50 c.c., add 10 grams. of silica, and 20 grams. of barium sulphate, and dry at  $100^{\circ}$  C. Powder the residue and extract it with warm ether; evaporate the ether and dissolve the residue in a little alcohol. Take 1 gram. of powdered hide which has been washed with alcohol, and dry at  $100^{\circ}$  C. Moisten it with a few drops of distilled water, and having added the alcoholic extract, allow the whole to macerate for half an hour. Filter through a square of cambric, previously dried and weighed, wash with alcohol, press out excess of liquid, and dry at  $100^{\circ}$  C. The increase in weight of the hide, multiplied by four, gives the oenontannin in one litre of the wine.

(b) *Estimation of Oenogallic acid.*

Dilute the alcoholic filtrate from the hide with distilled water to 100 c.c., and in 20 c.c. of this estimate the acid by means of a solution of iodine that has been previously standardised with gallic acid as follows:—

Prepare solution of iodine in potassium iodide containing 2 decigrams. of iodine per litre, and also a solution containing 0.125 gram. of gallic acid in 250 c.c. of distilled water. Mark a beaker at 50 c.c., place into it 10 c.c. of the gallic acid solution, and 3 c.c. of cold saturated solution of sodium bicarbonate. To this add the iodine drop by drop from a burette until a drop of the mixture, tested on thick filter paper dressed with powdered starch, leaves a stain surrounded by blue. Now add distilled water to the 50 c.c. mark and continue the addition of the iodine until a similar stain is again obtained. The amount of iodine thus used must be further corrected by making a blank

experiment on 50 c.c. of distilled water with 3 c.c. bicarbonate solution, and deducting the amount of iodine required to produce the stain. Having thus standardised the iodine, it is used in a similar manner on the 20 c.c. of the alcoholic liquid from the wine which has been previously neutralised with sodium bicarbonate.

(3) ESTIMATION OF COLOURING MATTER.

250 c.c. of the wine concentrated by evaporation (but without boiling) to 100 c.c. is rendered freely alkaline by ammonia, and then well shaken up precipitated arsenious sulphide. The whole is then filtered and washed with distilled water, and the filtrate having been rendered acid by acetic acid, to precipitate any sulphide of arsenic dissolved by the ammonia, is again filtered and washed. The two filters containing the sulphide of arsenic are digested on the water-bath in alcohol acidulated with acetic acid, and the whole having been again filtered, the residue is washed with hot alcohol until all the colouring matter is extracted. Finally, the alcoholic solution is evaporated in a tared capsule, desiccated at  $105^{\circ}\text{C}$ ., and the residual colouring matter is weighed.

III.—PREPARATION OF BUTTER FOR THE REFRACTOMETER.

The butter is melted in a porcelain capsule, and then beaten up with two or three pinches of fused and pulverised calcium chloride, which takes up the water and the casein. The whole is then kept warm until it settles, and the clear butter-fat is decanted off and filtered through a plug of cotton wool; the clear butter-fat is heated to  $60^{\circ}\text{C}$ . and placed in the prism of the instrument, and the reading is taken at the moment when the inner thermometer marks  $45^{\circ}\text{C}$ .

REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN  
ANALYTICAL PROCESS.

A DELICATE REACTION FOR CYTISINE. DR. J. VAN DE MOER. (*Ned. Tydschr v. Pharmacie*, etc. February, 1891.)—This alkaloid, obtained from the seeds of *Cytisus Laburnum*, has been supposed to be insoluble, or nearly so, in chloroform, but the author discovered this to be the solvent *par excellence*. This fact enabled him to extract the alkaloid in a far superior state of purity than before, and, as the result of a great many elementary analyses, he proposes the formula  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}$  instead of  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ . The author also has proved the identity of this alkaloid with ulexine, the active principle contained in the seeds of *Ulex Europaeus*. In case of poisoning with this alkaloid, the expert should test particularly the vomit and the urine; but in case of sub-cutaneous administration of small doses, the urine is the only material worth testing. Physiological experiments have proved the rapid elimination of the poison through the kidneys.

The toxicological analysis is performed according to Dragendorff's method, and advantage is taken of the solvent action of petroleum-ether, etc., on the accompanying impurities. After these have been removed, the old plan was to shake the alkaline solution with amylic alcohol, but this not being a good solvent, the author has replaced it by chloroform.

Although analysts could without difficulty isolate the alkaloid, all their trouble went for nothing, as there was no proper and reliable test for traces of this body.

The author has, however, been fortunate enough to discover a most delicate test, which plainly detects .00005 gram. of the poison.

The alkaloid is moistened with a drop of a weak solution of ferric-ammonium alum, which will give a reddish colour. On addition of a little hydrogen peroxide the colour disappears, but, particularly on warming, soon changes to a very persistent, splendid blue. If now moistened with ammonia (not potash or soda) the colour changes to a reddish violet, and the blue is restored by acids. No other alkaloid gave the reaction. The quantitative analysis is best done by titration with Mayer's solution. L. DE K.

ANALYSIS OF CRUDE GLYCERINES. F. FILSINGER. (*Chem. Zeit.*, No. 102, 1890.)—

A few years ago an estimation of the specific gravity, coupled with an ash determination, was all that was required; but these simple tests are, of course, of little use in determining the value of soap-leys. Apart from any mixtures, there are three different kinds of glycerine in the trade. 1. Saponification glycerine obtained from the few works where they still saponify fats with lime. This glycerine is characterised by a straw-yellow or brownish colour, of an agreeably sweet taste and absence of smell when rubbed on the hands. The reaction is generally neutral unless a little free lime should be present. This glycerine, which has an average specific gravity of 1.24, ought not to contain more than .5 per cent. of ash, and must remain fairly clear on addition of sub-acetate of lead or hydrochloric acid. Tested in Gerlach's apparatus it should show a boiling point of about 138°C. 2. Distillation glycerines, the product of the saponification of fats with sulphuric acid, with or without pressure. They are met in the trade in various states of purity. They have a burning, astringent taste which often hides the sweet one completely, smell nasty and leave often up to 3.5 per cent. of ash, consisting chiefly of salt and lime sulphate. On adding sub-acetate of lead there forms a voluminous precipitate, sometimes enough to gelatinise the whole. Hydrochloric acid often gives a copious, fusible precipitate, chiefly consisting of fatty matter. The boiling point is generally lower than 125°C. Even the best brands of these glycerines are about 10 per cent. lower in price than the worst saponification glycerines. 3. Soap-leys glycerine. This is the most impure of all, and has to be put through many processes before it can be distilled. When sold for that purpose it should have a brownish colour and contain no more than 10 per cent. of ash and 8 or 10 per cent. of water.

Now as far as analysis goes, a chemical one is not wanted for the pure glycerines. All that is needed is the estimation of the specific gravity with a gravity bottle or a Westphal balance, or the taking of the boiling point in Gerlach's apparatus. For the chemical analysis of impure samples, the only process which has stood the test for years is the permanganate method originally described by Benedikt and Zsigmondi.

The Acetin process devised by Benedikt and Cantor gives good results with very concentrated glycerines. Acrylic compounds do not interfere.

The author further communicates a process which has been in use for some years in a Hamburg laboratory. For the estimation of water, 20 grams. of the sample are put into a flask provided with a ground stopper and exposed for ten hours to a temperature of 100°C. The loss is taken as water. To estimate the fixed impurities, 5 grams.

of the sample are heated in a flat platinum dish up to  $180^{\circ}\text{C}$ , at which temperature the glycerine completely volatilises without perceptible charring. After cooling and weighing it is as well to once more heat to see if there be any further loss. To complete the analysis the ash may be taken. This simple process gives results quite accurate enough for technical purposes.

L. DE K.

ON THE ANALYSIS OF WHITE WAX. G. BUCHNER (*Chem. Zeit.*, No. 101, 1890).—Some two years ago the author called attention to the fact that a genuine sample of white wax may still show a too high saponification or acidity equivalent, if it has been bleached by chemical means. Although this does not frequently happen, analysts should, however, be careful in giving an unfavourable report without further testimony. The author's statement has been doubted by D. H. Röttger, who supposed he was not supplied with genuine samples; but experiments recently conducted by Messrs. Buisine prove the author to be in the right. In fact, the acidity equivalent of an undoubtedly genuine sample may come as high as 24, and its saponification number as high as 100.

L. DE K.

ESTIMATION OF CARBON IN IRON AND STEEL. L. RUPP (*Chem. Zeit.*, No. 102, 1890).—After some practice, an analyst may easily execute five analyses daily, by adopting the author's process. A few grams. of iron filings are put into Thörner's carbon apparatus, containing 40 c.c. of a hot solution of sulphate of copper. After the lapse of ten minutes, 50 c.c. of a saturated solution of chromic acid and 120 c.c. of *hydrated* sulphuric acid (saturated with chromic acid) are added, and the whole heated to  $80^{\circ}\text{C}$ . for about three quarters of an hour. To make sure of complete oxidation of the carbon, another 50 c.c. of this sulphuric acid are added, and the liquid heated to nearly boiling. After cooling somewhat, air is forced through the apparatus by means of an aspirator.

The apparatus consists of Thörner's boiling apparatus, connected with the usual chloride of calcium and soda-lime tubes. The air is passed at the rate of two or three bubbles per second through a wash bottle, containing sulphuric acid.

L. DE K.

ESTIMATION OF SULPHUR IN PIG LEAD. PROF. W. HAMPE (*Chem. Zeit.*, No. 105, 1890).—50 grams. of the finely divided sample are by degrees put into a crucible containing 100 grams. of fusing nitre. A spirit lamp should be used. The mass is constantly stirred with a bent glass rod until the oxidation is complete, which generally takes about one hour. The crucible is emptied whilst hot, and the mass extracted with boiling water. The solution is treated with carbonic acid until all the lead is precipitated and then filtered. After removing nitric compounds by evaporating with excess of hydrochloric acid, the sulphuric acid is precipitated with barium chloride.

The author has proved the accuracy of the process by experimenting on mixtures of pure lead and pure galena.

Another process communicated by the author, but which is rather too complicated for chemists employed in metallurgical works, consists in heating the metal in a current of chlorine, as in the analysis of grey copper ore. The metal is, however, never quite chlorinised, so, after removing the coating of chloride of lead, the operation must be



repeated. As some lead chloride gets into the absorption tube, the author recommends to first convert it into carbonate by boiling with excess of pure carbonate of soda. The filtrate containing the sulphuric acid is then acidified and precipitated with barium chloride.

L. DE K.

NOTE ON GLASER'S PROCESS FOR THE ESTIMATION OF IRON AND ALUMINA IN MANURES. D. TH. MEYER. (*Chem. Zeit.*, No. 102, 1890.)—A joint committee of German manure-makers and agricultural analysts, assembled last year in Bremen, has reported in favour of Glaser's spirit method instead of the ammonia and acetic acid process. That process cannot very well be defended. If too much acetic acid is added, the results are too low, and if the manure contains a fluoride, they will be too high. These sources of error do not occur in Glaser's process. The separation of the iron and alumina from the lime is very successful, and allows the latter to be very accurately determined. The gypsum takes, however, some time for complete separation. The drawback to Glaser's process is his complete ignoring of the magnesia. True, its sulphate is practically insoluble in absolute alcohol, but far from insoluble in a mixture of alcohol, water, and sulphuric acid. A fluid prepared by shaking 25 c.c. of absolute alcohol, 20 c.c. of water, and 5 c.c. of sulphuric acid with powdered Epsom salts, contained 3.2 per cent. of magnesia per 250 c.c. Suppose the sample to consist of pure magnesia, every trace of it would remain in the alcoholic fluid. Another experiment convinced the author of the co-precipitation of the magnesia with the iron and alumina. He twice analysed a solution of lime, iron, and aluminic phosphates, but in one case added sulphate of magnesia. The separated sulphate of lime proved to be pure, but in the second experiment the precipitated iron and alumina phosphates weighed three times heavier than in the first one. And a qualitative analysis proved this to be due to the presence of magnesia.

It is, therefore, not a matter of astonishment, that Glaser's method gives, as a rule, higher results than the conventional method, even if the manure should contain fluorides.

To see in how far the process can be trusted for commercial purposes, the author tried several Belgian phosphates. The magnesia was each time estimated by re-dissolving the precipitate in hydrochloric acid, boiling with some ferric chloride, and precipitating the excess of this, together with the phosphoric acid, with ammonia. The magnesia was then precipitated as usual with phosphate of soda.

Sample No. 1 : Obtained .63 per cent. of mixed iron and alumina ; but, after estimating the magnesia, this became reduced to .48 per cent.

Sample No. 2 : Obtained 4.23 per cent. After allowing for magnesia, only 4.15 per cent.

Sample No. 3 : Obtained 3.52 per cent. After allowing for magnesia, 3.12 per cent.

Of course, if the amount of magnesia in the manure is very trifling, no harm will be done ; but if large, it must seriously interfere with the accuracy of the process. Glaser's method is, therefore, not yet fit to become the recognised trade process, and is, in fact, at the moment, not much better than the old conventional one, unless one takes the trouble to estimate the co-precipitated magnesia.

L. DE K.

APPOINTMENT.—Dr. James Baynes, of Hull, has been elected to the post of Public Analyst for the City and Borough of Peterborough.

ERRATUM.—Mr. Cassal's paper on "Dyed Sugar" was unfortunately omitted from the list of papers read during 1896, contained in the retiring President's address in our last issue.

# THE ANALYST.

APRIL, 1891.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL meeting of the Society was held on the 4th March at Burlington House, the President, Mr. R. Hehner, in the chair.

The minutes of the previous meeting were read and confirmed.

On the ballot papers being opened, it was announced that the following gentlemen had been elected as members:—F. W. Babington, Inland Revenue Department, Ottawa; E. Russell Budden, London, Consulting Chemist; W. L. Hiepe, Ph.D., Manchester, Analytical Chemist; Thomas Hunter, Bristol, Analytical Chemist; Thomas Macfarlane, F.R.S. of Canada, Chief Analyst, Inland Revenue Department, Ottawa.

The following papers were read and discussed:—

“On Malt Vinegar,” by the President.

“The Werner-Schmid Method of Milk Analysis,” by Dr. T. Eustace Hill.

The next meeting will be held at Burlington House on Wednesday, the 1st April inst.

## ON THE COMPOSITION OF MILK AND MILK PRODUCTS.

BY DR. P. VIETH.

(Read at Meeting, February, 1891.)

For a number of years I have been in the habit of laying before you annual reports on the work done in the laboratory which is under my charge; the report for the year 1890 forms the subject matter of my present paper. (For former reports see *THE ANALYST*, vii. p. 53; viii. p. 33; ix. p. 56; x. p. 67; xi. p. 66; xii. p. 39; xiii. p. 46; xiv. p. 69; and xv. p. 44).

The total number of samples analysed in 1890 is 22,670, viz. :—

|        |                          |
|--------|--------------------------|
| 20,635 | samples of milk,         |
| 1,188  | „ cream,                 |
| 586    | „ skim milk,             |
| 40     | „ butter milk,           |
| 3      | „ whey,                  |
| 165    | „ butter and butter-fat, |
| 29     | „ water,                 |
| 24     | „ sundry articles,       |

Of the milk sample 11,816 were taken from the railway churns in which the milk arrived from the country. While part of this milk is kept back for the production of cream, the bulk of it is distributed with the least possible delay. In order to keep a constant control over the men entrusted with delivering the milk to the customers, 7,104 further samples were taken before, during, and after delivery, and submitted to analysis. The following table contains the monthly averages of the results referring to all these samples :—

AVERAGE COMPOSITION OF MILK.

| 1890.          | Samples taken |           |      |            |                  |                  |               |
|----------------|---------------|-----------|------|------------|------------------|------------------|---------------|
|                | On arrival.   |           |      |            | Before sent out. | During delivery. | After return. |
|                | Spec.Gravity  | Tot. Sol. | Fat. | Sol.n.Fat. | Tot. Sol.        | Tot Sol.         | Tot. Sol.     |
| January ..     | 1·0323        | 12·95     | 3·80 | 9 15       | 12·88            | 12·96            | 13·02         |
| February ..    | 1·0324        | 12·84     | 3·70 | 9·14       | 12·75            | 12·90            | 12·86         |
| March ..       | 1·0323        | 12·76     | 3·63 | 9·13       | 12·69            | 12·84            | 12·92         |
| April ..       | 1·0322        | 12·66     | 3·57 | 9·09       | 12·57            | 12·70            | 12·74         |
| May ..         | 1·0324        | 12·63     | 3·53 | 9·10       | 12·58            | 12·74            | 12·74         |
| June ..        | 1·0323        | 12·64     | 3·55 | 9·09       | 12·54            | 12·68            | 12·77         |
| July ..        | 1·0320        | 12·81     | 3·75 | 9·06       | 12·75            | 12·82            | 12·84         |
| August ..      | 1·0319        | 12·86     | 3·81 | 9·05       | 12·83            | 12·87            | 12·90         |
| September ..   | 1·0319        | 12·81     | 3·77 | 9·04       | 12·86            | 12·83            | 12·90         |
| October ..     | 1·0322        | 13·04     | 3·89 | 9·15       | 12·94            | 13·03            | 13·13         |
| November ..    | 1·0321        | 13·07     | 3·94 | 9·13       | 12·92            | 13·08            | 13·18         |
| December ..    | 1·0322        | 13·02     | 3·89 | 9·13       | 12·86            | 13·07            | 13·10         |
| Yearly Average | 1·0322        | 12·84     | 3·74 | 9·10       | 12·76            | 12·88            | 12·92         |

The results obtained in the year 1890 are in close concordance with those of former years, not only with regard to the yearly average composition, but also with regard to the variations which the quality of milk undergoes in the course of the year. The lowest percentages of total solids and fat was found, as usual, in the second, the highest in the fourth quarter of the year.

Considering that the circumstances under which the samples are taken can by no means be called very favourable, the agreement between the results referring to the several series of samples will, I think, be found satisfactory. Such differences as do

exist might be easily explained, but to do so on this occasion seems to me to be rather beyond the limit of this paper.

Cream samples were taken for analysis before the cream was sent out, and also while it was delivered to the customers. The total number of such samples was 1,010 and the average results of their analysis were as follows:—

## AVERAGE PERCENTAGE OF FAT IN CREAM.

| 1890.             | Samples taken    |                  |
|-------------------|------------------|------------------|
|                   | Before sent out. | During delivery. |
| January .. ..     | 46.0             | 45.3             |
| February .. ..    | 47.6             | 47.5             |
| March .. ..       | 48.7             | 48.6             |
| April .. ..       | 49.9             | 50.0             |
| May .. ..         | 49.6             | 49.3             |
| June .. ..        | 48.3             | 48.6             |
| July .. ..        | 47.7             | 47.3             |
| August .. ..      | 49.0             | 49.2             |
| September .. ..   | 49.5             | 50.3             |
| October .. ..     | 50.5             | 50.4             |
| November .. ..    | 46.5             | 47.0             |
| December ... ..   | 46.8             | 46.9             |
| Yearly average .. | 48.3             | 48.4             |

Clotted cream, of which 51 samples were analysed, was of the following average composition:—

|                               |                 |
|-------------------------------|-----------------|
| Water .. ..                   | 35.16 per cent. |
| Fat .. ..                     | 58.35 „         |
| Proteids and Milk Sugar .. .. | 5.97 „          |
| Ash .. ..                     | .52 „           |

Skim milk, resulting when cream was separated from milk by means of centrifugal cream separators, contained, as a rule, from .2 to .4 per cent. of fat.

I do not think it necessary to give the figures relating to the analysis of 103 samples of butter, as these results, with the exception of those obtained in December, were included in a paper which I read before this Society two months ago (*THE ANALYST*, xvi. p. 1). On that occasion, however, I did not refer to the examination of the clarified butter-fat. The volatile acids—Wollny figures—found in the several classes of butter in 1890 were as follows:—

|                |                     |           |
|----------------|---------------------|-----------|
| English butter | 25.3 — 30.0 average | 27.6 c.c. |
| French „       | 25.6 — 30.8 „       | 28.7 „    |
| Kiel „         | 21.3 — 30.7 „       | 27.7 „    |
| Danish „       | 27.3 — 29.9 „       | 28.8 „    |

The figures fall below what is considered the limit in four cases of Kiel butter derived from two large well-known and managed dairies in Holstein—I will call them A and B—the same which turned out butter with low volatile acids in 1889. There were

three abnormal samples from dairy A, the results being 24·2, 22·0, and 21·3, and one abnormal sample from dairy B, the result being 23·7. The low results were found during the time from July to October, *i.e.*, at the same period of the year at which low volatile acids were observed in 1889.

When speaking on this matter last year a good deal of incredulity or, at any rate, suspicion was displayed with regard to the genuineness of the butter in question. Among others the question was asked, whether it was not a fact, that the volatile acids were found to be low at a time when butter prices were high. This was not the case either in 1889, or in 1890. In the former year butter prices were below the average for the year, from beginning of April to end of September, and in the latter again from beginning of April to end of August, while in both years the highest prices were paid in March and in December. There is, then, no coincidence whatever between low volatile acids and high butter prices, and vice versa, and even if there had been, I should never have held that the latter stood in any connection with, or explained the former in the cases in question.

The matter seemed to me of sufficient interest and importance to cause my friend, Dr. Schrodt, principal of the Dairy Experimental Station at Kiel, to follow it up. The proprietor of dairy A willingly agreed to send a sample of butter to Kiel for examination once a week, and he has done so since beginning of May. Dr. Schrodt informs me, that with the progress of the period of lactation the volatile acids decreased reaching their lowest point in October, and that with the beginning of calving season in November they at once increased and quickly rose above 25.

I will here put together all my results referring to butter from this particular dairy and add, with Dr. Schrodt's permission, those of his results which he has communicated to me in corroboration of my own.

Results obtained in London :—

1889. June, 27·6; July, 25·9, 24·7; August, 24·2; October, 22·8; November, 21·1; Dec., 29·2, 29·3.

1890. July, 24·2; October, 22·0, 21·3; Nov., 26·2

Results obtained in Kiel :—

1890. July, 24·6, 24·7, 24·0, 24·0; October, 23·0, 21·6, 22·2, 23·1; November, 26·2, 26·6, 27·0, 27·1; December, 27·3.

I may remark that results obtained in London ought to be compared with those obtained in Kiel about a fortnight previous. I once more express my firm conviction that in this instance we have to deal with a decrease in volatile acids below the usual limit, which has to be put down entirely to natural causes.

I have mentioned on several previous occasions another case of naturally low volatile acids; I refer to butter-fat derived from the milk of cows kept at the Aylesbury Dairy Company's farm near Horsham. Of such butter-fat thirty-two samples were examined during the past year with the result, that the Wollny figures were found to be below 25 from January to middle of April, and again from August to November. During the remaining parts of the year they varied from 25 to 26. The observed extremes were 22·1 and 26·2.

In butter-fat which had been exposed to the action of air and light for eighteen

months and become bleached, the volatile acid figures had increased from 29·2 in the original to 30·4 in the bleached sample.

A decrease of volatile acids was observed in butter which had been kept for more than ten years. A glass and a stoneware jar filled with such butter were accidentally found and their contents examined. In both jars the bottom layers of butter appeared fairly well preserved. In the glass jar the top layer was extremely rancid, but contained no visible fungi; in the stoneware jar the butter had no particular smell, but was covered with a thick green fungous growth, and red fungi had penetrated the upper layer to a depth of about two inches. The results of the examination were as follows:—

|                             |    |    |                                  |
|-----------------------------|----|----|----------------------------------|
| Glass jar, bottom layer     | .. | .. | 26·2 c.c. $\frac{N}{10}$ alkali. |
| " " top "                   | .. | .. | 25·6                             |
| Stoneware jar, bottom layer | .. | .. | 25·7                             |
| " " top "                   | .. | .. | 21·2 "                           |

These results fully agree with similar ones which I submitted to you five years ago (THE ANALYST, xi. p. 70).

Turning once more to the subject of milk, I wish to relate some experiments which I have made with regard to freezing milk. Two gallons of milk were put into an oblong tin vessel, ten inches in height, a tight-fitting lid screwed on, the vessel put in a refrigerated salt solution, and kept therein at a temperature of 14°F. for three hours. Preliminary experiments had shown that after that length of time the mass of ice formed did, apparently, not further increase. On examination it was found that ice was formed at the bottom and sides of the vessel, and that a funnel-shaped cave in the centre was filled with liquid. This liquid was poured off, and a sample of it analysed, as were also samples of ice taken from the top and bottom layer. The results were as follows:—

|              |     | Ice.   |            | Liquid Part.    |
|--------------|-----|--------|------------|-----------------|
|              |     | Cream. | Skim milk. |                 |
| Total solids | ... | 25·30  | 7·86       | 19·58 per cent. |
| Fat          | ... | 18·94  | ·68        | 5·44 "          |
| Ash          | ... | ·53    | ·62        | 1·11 "          |
| Sol. n. fat  | ... | 6·36   | 7·18       | 14·14 "         |

The experiment was repeated, care being taken to drain off the part which remained liquid as completely as possible, and to carefully separate the frozen cream from the frozen skim milk. The following were the results of the examination:—

|               |     | Ice.   |            | Liquid Part.    |
|---------------|-----|--------|------------|-----------------|
|               |     | Cream. | Skim milk. |                 |
| Proportion    | ... | 8·8    | 64·7       | 26·5 per cent.  |
| Spec. Gravity | ... | 1·0100 | 1·0275     | 1·0525          |
| Composition:  |     |        |            |                 |
| Water         | ... | 74·44  | 92·10      | 80·54 per cent. |
| Fat           | ... | 19·23  | ·68        | 5·17 "          |
| Proteids      | ... | 2·64   | 2·80       | 5·38 "          |
| Milk Sugar    | ... | 3·33   | 3·95       | 7·77 "          |
| Ash           | ... | ·52    | ·60        | 1·18 "          |

100·16

100·13

100·04

These figures prove what has been shown on previous occasions, that frozen milk contains a much higher proportion of water than the original milk in which the ice was formed, and that the part remaining liquid is a concentrated milk.

The ice is by no means a solid mass, but a conglomerate of crystalline plates. The fact that the latter, when examined singly, are found to be quite clear, proves that fat globules do not enter into the crystals. The component parts of the "Solids not fat" seem to participate in the formation of the crystals in about the same relative proportion in which they are present in the milk. This was so, at least, in the case to which my remarks refer, the relative proportions of proteids, sugar, and ash being found as follows :—

|          |     | Cream. | Ice. | Skim milk. | Liquid Part. |
|----------|-----|--------|------|------------|--------------|
| Proteids | ... | 40·68  |      | 38·10      | 37·55        |
| Sugar    | ... | 51·31  |      | 53·74      | 54·23        |
| Ash ..   | ... | 8·01   |      | 8·16       | 8·22         |

The behaviour of milk, when exposed to low temperatures, is not without interest in itself, but apart from this it is also of some practical importance. People who are ignorant of what is actually taking place when milk freezes would naturally see no harm in melting milk ice and using the liquid obtained as milk. If a milk vendor would proceed in this way he might easily get into trouble.

#### DISCUSSION.

The PRESIDENT said that Dr. Vieth had added to the debt they already owed him. His papers were not only welcome to this Society, but were looked forward to with interest by all interested in dairy matters in England and abroad.

Dr. MUTER said he quite confirmed Dr. Vieth's results about frozen milk. During the long frost in January he had occasion to examine the contents of a frozen churn as delivered at the railway station. The following were the results :—

#### (1) Milk passing through strainer :—

|                |    |    |    |    |       |
|----------------|----|----|----|----|-------|
| Total solids   | .. | .. | .. | .. | 12·80 |
| Fat            | .. | .. | .. | .. | 3·80  |
| Solids-not-fat | .. | .. | .. | .. | 9·00  |

#### (2) Contents of strainer :—

|                |    |    |    |    |      |
|----------------|----|----|----|----|------|
| Total solids   | .. | .. | .. | .. | 9·28 |
| Fat            | .. | .. | .. | .. | 2·63 |
| Solids-not-fat | .. | .. | .. | .. | 6·65 |

#### (3) Ice off churn lid :—

|                |    |    |    |    |      |
|----------------|----|----|----|----|------|
| Total solids   | .. | .. | .. | .. | 4·94 |
| Fat            | .. | .. | .. | .. | 1·70 |
| Solids-not-fat | .. | .. | .. | .. | 3·24 |

It was evident, therefore, that unless very carefully thawed and mixed frozen milk might present most anomalous results.

Mr. FABER inquired if Dr. Vieth had any information about the way the cows had been kept, and whether the feeding of them had anything to do with the analysis of the butter-fat, and as to the cows having recently calved or otherwise.

Dr. DUPRE asked if Dr. Vieth had ever compared the volatile acid with the total soluble acids; whether there was anything in the shape of compensation going on, whether when the one increased the other diminished, or *vice versa*.

Mr. YOUNG said he had always taken the estimation of the ash, which he considered of great importance, and a large number of ash estimations would make Dr. Vieth's figures very valuable indeed. Mr. Young also mentioned that large quantities of milk were frozen into blocks for the large shipping companies who used them as required for their passengers. It was evident from Dr. Vieth's experiments that if these blocks were used in portions the milk supply on board ship must vary much in quality.

The PRESIDENT remarked that presumably Dr. Vieth's fat determinations were made by the plaster method; he asked what number of cows had yielded the abnormal samples of milk referred to? In his experience there was a direct connection between the price of butter and the proportion of volatile acids. He found that when butter prices went up the number of samples that yielded an abnormally low proportion of volatile acid at once went up, that is to say, that the practice of adulteration was closely connected with the market price. It was a most striking circumstance that when butter was dear whole series of samples analysed by him fell either just upon or slightly below the Reichert limit, and he could not but conclude that foreign shippers sometimes let their produce down as low as they could without much risk of prosecution. Of course, there could not be any connection between price and the proportion of volatile acids in undoubtedly genuine samples.

DR. VEITH, in reply, said the butter showing the low results was made at a large farm where about 200 cows were kept. At the time when the abnormal results were observed the cows were fed on pasture land which was reclaimed from the sea. Dr. Schroot was under the impression that the abnormal results had nothing to do with the feed. With regard to the connection between low volatile acids and butter prices hinted at by Mr. Hehner last year, he did not think it was meant seriously, but he now saw it was as Mr. Hehner said he found it so. His (Dr. Vieth's) experience went the other way. He had during the last three years analysed a great number of samples chiefly from France, Holstein, Denmark, and Sweden, and had never found any definite connection between the prices of butter and the quantity of volatile acids. The composition of frozen milk was certainly of considerable interest. As to frozen milk being used on board ship, he knew of that long ago, but he could not understand how milk could be frozen in blocks. He had never seen milk entirely frozen; there was always a certain quantity of liquid left which would not freeze, just as it was the case with sugar and salt solutions. With regard to the ash, he must say that it was not determined in the samples referred to in the paper in which sp. gr. and solids were determined and the fat calculated. He made, of course, a great number of ash determinations, but could not see much use in bring them forward because they simply proved what he had stated on previous occasions, viz., that the ash of normal milk was as near as possible 8 per cent. of the solids-not-fat.

### THE WERNER-SCHMID METHOD OF MILK ANALYSIS

By T. EUSTACE HILL, M.B., B.Sc., A.I.C., Medical Officer of Health, South Shields.

(Read at the Meeting, March, 1891.)

IN the ANALYST of 1889, and again in the *Chemical News* of November of the same year, there appeared some very interesting remarks and facts by Mr. Stokes concerning a new process for the rapid estimation of fat in milk, first mentioned by Dr. Werner-Schmid in the *Zeitschrift für Analytische Chemie*, vol. xxvii., part iv.

Mr. Stokes, after detailing the process as originally carried out by Dr. Schmid, pointed out how it could be improved, and gave a very favourable experience of its working as carried out with his modifications. The process appeared so simple and



short, and the results published by Mr. Stokes so good when compared with calculated results, that I determined to give it an extended trial, and during the last eighteen months have determined the fat in over 200 different milks by this method, with the result of being able to corroborate Mr. Stokes as to its accuracy, simplicity, and rapidity, as regards all of which it compares favourably with, and, I think, even excels any other process for the estimation of fat in milk.

Apart from its rapidity, the process has the great advantage of being equally applicable to fresh or sour milks, however advanced in decomposition, and it is quite possible to complete the determination of the fat of many samples in the time required for estimating the total solids. I have frequently made complete analysis of six samples of milk in one morning, and however convenient and useful it may be in most cases to estimate the fat by calculation by means of the sp. gr. and total solids, I think it will be agreed that it is more satisfactory and safe in every way to know the percentage of fat by actual analysis. For myself I should be very unwilling to take a milk case into court with only a knowledge of the fat from calculation tables. This process, however, requires no more time and but little more trouble than has to be given in the determination of the sp. gr. and total solids.

Dr. Schmid's method is as follows—10 c.c. milk is pipetted into a test tube holding rather more than 50 c.c., and graduated in tenths of a c.c., 10 c.c. of strong HCl are then added, the mixture is shaken and boiled till it turns dark brown, and then it is cooled by placing the tube in cold water. 30 c.c. of ether is then added, and the whole shaken and allowed to stand, when in a short time the ether separates clear, and is measured. 10 c.c. is then pipetted off into a dish and evaporated, and the residual fat weighed and calculated for the original quantity of the ethereal solution. Mr. Stokes in the *ANALYST*, February, 1889, points out how the above process can be improved, and in the *Chemical News*, November, 1889, gives a full account of it as finally modified and worked in his own laboratory.

Into special tubes he pipettes 10 c.c. of the milk, or if sour weighs 10 grams. and with 10 c.c. strong HCl from a wash bottle detaches any particles of milk that may adhere to the side of the tube. He boils, with frequent shaking, till the mixture of milk and HCl turns brown, and then lets it stand for three minutes before cooling by plunging the tube into cold water. He then fills up with ether roughly to 50 c.c. mark, shakes well for half a minute, and allows to settle for five minutes, after which he pipettes off 20 c.c. of ethereal solution into a weighed dish, evaporates, dries in air bath, and weighs residual fat. The number of c.c.'s of ether remaining in the tube is then read together with three-fourths of a fluffy-looking stratum immediately beneath the ether, and these added to the 20 c.c. ether evaporated give the total number c.c. of ether to be considered in calculating the percentage of fat. A correction for sp. gr. has, of course, to be made in each case.

When I first practised this process according to Werner-Schmid's directions, I was inclined to be dissatisfied, as the results were anything but accurate, owing chiefly to the fluffy layer below the ether being disregarded, which consists chiefly of ether mixed with a little HCl and altered casein. The ether I used also was unwashed, which influences the results considerably.

When Mr. Stokes' paper on the process, however, appeared in the *Chemical News* I gave the process another trial with much more satisfactory results.

I determined the fat of every milk I subjected to the Werner-Schmid method by Adams' paper coil method, using fat free coils, as that method has been approved by the Society of Public Analysts, and the fat obtained by it can be taken as a standard. All my results are, therefore, compared with the results obtained by Adams' method, and not with calculated results, as I consider the former a better plan. At first my results were constantly about 15 per cent. below those obtained from the same milk by Adams' method, which I ultimately found was partly owing to the different way milks drained from the pipette, as compared with each other, and also with water. For instance, 10 c.c. of a milk with a sp. gr. 1.030 would weigh not 10.3 grams., but perhaps 10.10 grams., and this in a pipette which was correctly graduated for delivering 10 c.c. of water. This difficulty I obviated by weighing the milk into the tubes, which, though more tedious, is certainly more accurate than by delivering from a pipette. I also found, contrary to Mr. Stokes' experience, that it was necessary to wash the ether, otherwise the results came out at least .05 per cent. too low. By weighing the milk before adding the HCl, and also using washed ether, I can constantly obtain results which differ from those obtained from the same milk by Adams' method, only within the limits of experimental error, say (+ - .04). I obtained the same results whether the mixture of acid and milk be boiled, as is deemed necessary by Mr. Stokes, or the tube is immersed in boiling water for five minutes, shaking every now and then. I prefer the latter operation, as the tubes supplied by Messrs. Townson and Mercer are too thick to stand heating by the naked flame without danger of cracking. These tubes, which should be made of thinner glass, are graduated to half a c.c. from 20 - 50 c.c., and it is important that the accuracy of the graduation be proved.

I find it to be much easier and equally accurate to pipette off 15 c.c. of ether instead of 20 c.c., as recommended by Mr. Stokes, especially in warm weather, when it is extremely difficult to pipette off 20 c.c. without getting some of the liquid beneath the ether layer into the pipette. Five minutes' drying of the fat in the water oven is quite sufficient after the ether has evaporated. The calculation is very easy; for instance, if the total ethereal solution +  $\frac{3}{4}$  of fluffy-looking stratum measure 26 c.c., and 15 c.c. produce .25 gram. fat, the percentage of fat in the milk will be

$$\frac{.25 \times 26 \times 10}{15} = 4.33 \text{ per cent. fat if 10 grams. of milk be taken.}$$

Below are some of the results obtained by this process and by Adams'. The samples were mostly taken under the Food and Drugs Act, and comprise milk from widely different sources, and are fairly representative of the agreement between the two processes.

|     | Werner-Schmid. | Adams. | Difference. |
|-----|----------------|--------|-------------|
| 1.  | 3.55           | 3.60   | -.05        |
| 2.  | 3.58           | 3.53   | +.03        |
| 3.  | 3.21           | 3.21   | 0.00        |
| 4.  | 3.53           | 3.57   | -.04        |
| 5.  | 3.96           | 3.97   | -.01        |
| 6.  | 3.57           | 3.60   | -.03        |
| 7.  | 3.31           | 3.38   | -.07        |
| 8.  | 3.09           | 3.08   | +.01        |
| 9.  | 3.16           | 3.14   | +.02        |
| 10. | 3.18           | 3.15   | +.03        |
| 11. | 3.24           | 3.23   | +.01        |
| 12. | 3.54           | 3.49   | +.05        |

These are not results that are picked out on account of their agreement, but represent twelve consecutive analyses of different milks, and with care the difference between the results should not be greater than is seen here.

With sour milks the results obtained cannot be compared with Adams' process, which is not applicable to milks that have curdled, but from '30 to '40 per cent. more fat is obtained by Werner-Schmid's method than by the one recommended by Bell for sour milks.

I determined the fat in one milk, which contained 3.53 per cent. of fat when fresh, after standing for three weeks, and obtained 3.56 per cent. of fat; while from another sample I obtained 3.29 per cent of fat after standing a month, the milk when fresh containing 3.24 per cent. of fat.

With condensed milks (unsweetened) the process is apparently satisfactory, for two separate determinations of the same milk (taking 2 grams. of the milk and making up to 10 c.c. with water) gave 11.57 and 11.60 per cent. of fat as compared with 11.46 by the Gerber-Ritthausen method, but the process is certainly not adapted for estimating the fat in the sweetened condensed milk owing apparently to the HCl acting on the sugar and producing a dark caramel-like substance, which is soluble in ether, and therefore gives too high results. I analysed several varieties of sweetened condensed milks, but in every case the results came out too high, as will be seen by the following figures:—

|    | Werner-Schmid. | Adams. |
|----|----------------|--------|
| 1. | 11.95          | 11.49  |
| 2. | 10.02          | 8.78   |
| 3. | 3.31           | 2.76   |
| 4. | 2.99           | 2.54   |
| 5. | 2.34           | 1.90   |

The last three samples are skimmed condensed milks. The fat obtained by the Werner-Schmid process in all the above samples had a dark brown appearance, showing the presence of some substance connected with the decomposition of the cane-sugar. In order to get over the difficulty I tried petroleum ether as the solvent instead of ether, but without success, for on shaking (and the same applies to the analysis of fresh milk) the contents of the tube unite into a gelatinous mass, which is more or less permanent.

I quite agree with Mr. Stokes, that the personal equation does not at all influence the result, for on many occasions Mr. Liverseege, assistant to the public analyst for Birmingham, and to whom I am much indebted for assistance, has obtained results agreeing with my own from the same sample of milk, and in the majority of cases he was responsible for the analysis by the Adams' method, with which the results by Werner-Schmid's method so well agree; but it is a process that requires some little practice before accurate results can always be obtained.

It is so accurate, and the saving of time so great, that it is to be hoped in the future it will receive a better trial than has hitherto been given to it.

I may say that the ether apparently dissolves out the whole of the fat from the acid mixture, for after well shaking I have been unable to detect any fat except in solution in the ether. The fat when dry, previous to weighing, is quite pure and free from acid if the process is properly carried out.

## DISCUSSION.

Mr. STOKES stated that he was very pleased to find Dr. Hill's results confirm the statements he (Mr. Stokes) first made in the ANALYST, XIV., 29, and more fully and accurately in the *Chemical News* of November 1st, 1889. Theoretically, a process that dealt with milk as a liquid was the best; since of any substance a gas was that which offered the largest surface, a liquid came next, and the very worst of all for extraction was a solid. Usually analysts reduced the milk from its natural second-best form, a liquid, and made it into the worst form, a solid, and then tried to extract fat from it. Theory, however, is not enough. Mr. Stokes, after trying practically every method of fat-extraction he had ever read of, had now for the last two and a half years used this method in preference to every other. He had done some thousands of fat-extractions thereby, with an almost invariable agreement between these and the calculated fat as determined by total solids and specific gravity, shown in the admirable tables of Messrs. Hehner and Richmond (ANALYST, XIII., 26.) Other methods that he had found to give equally good results were the Lactocrite, the Adams paper-coil, and the plaster process; only the labour involved and the time taken was greater with these. These processes, too, were quite inapplicable for stale milks or for sweetened condensed milks, while the Werner-Schmid method worked perfectly with these. Dr. Hill was mistaken in thinking his results were too high in working on sweetened condensed milks. It is true, a little caramel, sufficient to colour the ether, is taken up, but this does not appreciably add to the weight of the fat. Dr. Hill uses only the old form of tube, and so works to a disadvantage. In the new form of tube that Mr. Stokes introduced, the tube is narrowed for six inches in the middle of its length; this enables ether to be drawn off almost entirely, and gives very accurate readings of the small quantity of ether left in the tube. At present he knew of eight public analysts who habitually used this method. To secure accurate agreement between fat so determined and the calculated-fat, it is necessary to be sure that the total solids are quite dry, and to take the sp. gr. by the Westphal balance, or by the bottle. In the latter case the milk should be left for at least ten minutes after shaking, else air-bubbles will be weighed as milk. The lactometers generally used are not finely enough graduated for such critical sp. gr.

Mr. ALLEN said he was happy to be able to endorse almost every word that had fallen from the writer of the paper and Mr. Stokes—in fact, he was indebted to Mr. Stokes for instructing himself and Mr. Chattaway as to his way of working the Werner-Schmidt process of fat determination. He had the highest opinion of the method. He had checked it against the coil process, and was satisfied with the results. On the other hand, there were one or two disadvantages in the practical method of working adopted by Mr. Stokes, which he had done his best to improve, and, he thought, with some success.

In the first place, Mr. Stokes had an objection to the wide tube, and had drawn on the board a sketch of the tube he preferred. Working as Mr. Stokes did, that undoubtedly was a desirable improvement. Working as he (Mr. Allen) did, he had gone back to the old tube. He did not like the practice of drawing off a fractional part of the ethereal layer, and the subsequent calculation it involved. He proposed to draw off the whole of the ether, and then evaporate it in a flask or beaker. He objected to the

use of a dish for the evaporation of ethereal solutions of fats, for there was always a tendency to creep up the sides. In practice, the Adams process was liked in his laboratory quite as well as the Werner-Schmidt method, as it looked after itself; but the latter had the advantage of rapidity, and was better adapted for use with sour milk. He had also used it quite successfully for the estimation of fat in condensed milk, but had not tried it on sweetened condensed milk, and had not therefore met with the difficulty mentioned by Dr. Hill.

Mr. Allen said he commended to the notice of the Society the little arrangement he exhibited. It was devised by Mr. Chattaway, and was exceedingly useful for separating an ethereal layer from an aqueous liquid.

Dr. VIETH said that the author of the paper under discussion did not like to use 10 c.c. of milk, but preferred to weigh 10 grams. He himself thought it quite as well to measure the milk; it was certainly more convenient, and by using specially-gauged pipettes, he had never any difficulty in doing it sufficiently accurate. One thing struck him, and that was that, in the hands of those gentlemen who had taken up the process, the latter did really more than the inventor of the process professed it would do. Dr. Werner-Schmid said "the results compared favourably with the gravimetric process." That was years ago, when he (Dr. Vieth) believed the Adams process had not been taken up generally. What he thought it was compared with was something like the Soxhlet process, and as the Adams process professed to extract more fat than the Soxhlet process, the gentlemen working the process at the present time must get about 25 per cent. fat more than Mr. Schmid got himself. With regard to taking the specific gravity, he really thought using the lactometer was the most convenient way. If the milk were properly handled, and a correct instrument, with sufficiently large divisions, used, he did not see why the sp. gr. determination by means of the lactometer should not be quite sufficient, at any rate for a process like the one described in the paper. As to fat calculated and determined, he was not astonished to see the figures agree at this time of year, but he did not see how they could agree so well during the warmer time of the year, and when working on samples which were not quite fresh. Long before milk curdles it contains an appreciable quantity of lactic acid. In such samples the total solids are found considerably lower, and a calculation of the fat must necessarily lead to wrong results.

Dr. Vieth exhibited a new form of lacto-butyrometer, brought out by Dr. Gerber, of Zurich, last year, and described the way of using it.

Mr. DAVIES said that for a considerable time this process had been in use in his laboratory, and he had examined a large number of milks by it; he had entirely satisfied himself as to the reliance that could be placed on the process. It was an extremely rapid one, and compared favourably with the Adams process, and with the results of the calculations. The specific gravity was invariably taken usually by the bottle, but latterly by the Westphal balance, and whether this process or the Adams process was used, the results in his opinion were concordant. He did not agree with Dr. Vieth that it was always near enough to use a pipette. He had found that the weight of milk delivered from a 10 c.c. pipette was not always such as would be expected from the sp. gr., and sometimes was less than 10 grams. This was, no doubt, due to presence of air-bubbles remaining from the shaking that was necessary before pipetting off the milk. His practice was to weigh 10 grams in one of the Werner-Schmid tubes, and with tubes of the original form the results obtained were extremely satisfactory.

Mr. CASSAL said he certainly thought that when one process was being compared with another weighed quantities ought to be operated on. Everyone would agree

with Dr. Hill that it was improper to base prosecution cases upon analyses in which the fats had been calculated. When the fat was determined by the Adams process, worked in such a way as to eliminate all chances of error, he had always found that the results agreed very closely with those obtained by calculation, but for obvious reasons all prosecution cases should be based on actual determinations. He was in no way disposed to disparage the Werner-Schmid method. It was, no doubt, a very valuable process; but he was inclined to think that the Adams process when properly carried out was upon the whole more reliable and more satisfactory. He admitted that a longer time might be required—that is, that a greater length of time might elapse before the fat could be obtained and weighed—but the process was more automatic. The Werner-Schmid process required more personal attention. There were several sources of error in it of such a nature as to require very special precautions. In reference to the analysis of condensed milk, Mr. Cassal contended that when these contained large percentages of cane sugar, an accurate estimation of the fat could only be effected after removal of the sugar, which was best carried out by diluting a weighed portion of the sample, precipitating and filtering and determining the fat in the precipitated solids.

The PRESIDENT (Mr. Hehner) in summing up the discussion, said the subject of milk analysis was one of which every member thought he knew something more than anyone else did. We were now in a position to estimate fat with fairly quantitative accuracy, and counted the differences between the best methods only by hundredths of percentages. He thought that as regards the agreement between an actual result and a calculated quantity ideas of exaggerated accuracy should be avoided, as the specific gravity of solids-not-fat was, as a matter of necessity, subject to slight fluctuations. The Adams process had in the hands of most analysts proved everything that could be desired in point of accuracy and expeditiousness, and for his part he could not imagine any cases in which a saving of ten minutes, or even of half an hour, was of any consequence. The contraction of paper coils was an automatic operation, requiring the least possible amount of attention. As regards sour, or even decayed milk, he would raise a protest, as he had done on previous occasions, against their analysis. It was demonstrated to be impossible to estimate the amount of solids-not-fat in a sour or fermenting milk, and this being so, the cases in which the exact estimation of fat was of any consequence in old samples could occur but most rarely. Public analysts should invariably refuse to analyse old and decomposing milk samples, and leave them to those who pretended to be able to deal with them. A pipette nominally delivering five cubic centimetres of water never delivered five grams. of milk, and he preferred in every case to weigh the quantity of milk discharged. The estimation of the specific gravity, being of the utmost importance, should be treated with the same care as was bestowed upon other quantitative operations. A well-constructed lactometer was capable of giving accurate results, but public analysts never had a sufficient quantity of milk to employ such an instrument, as had already been pointed out by Mr. Stokes. Referring to the determination of fat in condensed milk, he did not feel sure that the higher results obtained by the Schmid method were really due to caramel-like products, for in the case of sugared milks it was necessary to dilute largely before spreading the solution on a paper coil, and in consequence but very minute quantities of condensed milk could be taken for each experiment, thus increasing the sources of error as far as the Adams process was concerned. He preferred to precipitate the casein and fat with sulphate of copper and alkali, and to extract the fat from the precipitate, as larger quantities of condensed milk could thus be dealt with. The discussion had been an instructive and profitable one, and the Society owed their thanks to Dr. Hill and to those who had assisted in the discussion.

*(Conclusion of the Society's Proceedings.)*

## REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESS.

DETECTION OF ROSIN IN BEES-WAX. H. RÖTTGER (*Chem. Zeit.* No. 4, 91).—

*Donath's process*: If a sample containing 5-10 per cent. of rosin is heated up to 110° C, a strong smell of turpentine will be noticed. But pure wax collected in the neighbourhood of pine woods also emits this odour. If large quantities of rosin are present, any dealer will at once notice this from the very appearance, but small percentages are best detected as follows: if rosin is boiled for some time with strong nitric acid it is gradually dissolved with evolution of nitric vapours. Water being added, a yellowish flocculent precipitate is obtained, which is not altered by fixed alkalis, but dissolved in ammonia with a blood-red colour. A nut-sized piece of the wax is therefore boiled in a test-tube with strong nitric acid for fifteen minutes. A little cold water is carefully added to solidify the layer of wax, so as to enable to pour off the acid fluid. On cooling, or better still, an addition of more water, a precipitate is obtained which gives the characteristic reaction with ammonia. *E. Schmidt's process*: 5 grams. of the sample are boiled in a flask with 25 grams. of common nitric acid of 1.33 sp. gravity for one minute. An equal volume of cold water is then added, and then ammonia in slight excess. If now the fluid is poured off from the wax into a cylindric glass, the colour will be yellowish if the wax were pure; but if adulterated with rosin, even with only 1 per cent., the colour will be reddish-brown. It is as well to test a pure sample side by side. *Hager's process*: The sample is boiled with 15 times its weight of dilute alcohol (two alcohol and one water). After cooling, the liquid is poured, or, if necessary, filtered off, and then diluted with an equal bulk of water. If rosin is present the liquid turns milky. Stearic acid does not interfere with this test. The German Pharmaceutical Committee recommends to boil the suspected wax with 10 parts of water and three parts of carbonate of soda for 15 minutes. If rosin is present a persistent emulsion is obtained. Sedra proposes the following process: 3 grams. of the sample are dissolved in a test-glass in 30 c.c. of chloroform, and then shaken with 200 c.c. of lime-water. Pure wax will cause an emulsion, but if rosin is present a turbid yellowish-brown liquid separates out. The author, after trying these processes, utterly condemns the last process, as he failed to discover an admixture of even 20 per cent. of rosin. Hager's process gives satisfactory results, but the author finds that this chemist makes a mistake in supposing the weak alcohol not to affect the wax or any stearic acid which may be present. Traces of these bodies are dissolved, but are distinguished from rosin by quickly collecting on the surface of the diluted fluid. If, however, proof spirit is used, the stearic acid is practically left undissolved, and even 2 per cent. of rosin may be detected. The best plan is, however, to first thoroughly boil the sample with strong alcohol, to evaporate the alcoholic solution, and then to apply Donath's nitric acid and ammonia test.

L. DE K.

**THE ASSAY OF INDIGO.** DR. FRITZ VOELLER. (*Zeitschr. f. Angew. Chemie.* No. 4, 91).—The process most commonly employed is the one with permanganate, proposed by Fr. Mohr. The results are, however, often very inaccurate, especially with the inferior kinds of indigo, as these mostly contain other organic compounds, which are also

oxidised by permanganate. The traders, knowing this, do not scruple to even employ oxalic acid as an adulterant. Another drawback to the process is the difficulty of properly noticing the end reaction on titrating. The same may be said of other processes based on oxidation, such as Bolley's process with hydrochloric acid and chloride of lime or chlorate of potash, Penny's process with sulphuric acid and chromate of potash, or Ullgreen's method with red prussiate of potash. Chevreuil's process and other similar colour-methods are not criticised, although they do occasionally good service, they can scarcely be classed among the *analytical* methods.

The reduction processes of Pugh, with sulphate of iron and soda-ley, and Fritsche, with glucose, alkalis, and alcohol, whose objects are to reduce the indigo to indigo-white, which may then be re-oxidised and finally weighed, are also likely to give too favourable results, as there is always a chance of the co-precipitation of foreign organic bodies, unless these have been first removed by suitable means. Berzelius found that, besides indigo-blue and some mineral matter, the commercial product contains three other bodies, which he called indigo-gluten, indigo-red, and indigo-brown. The first, which may be extracted with dilute acids, is closely related to vegetable albumen, and precipitated from its solution by alcohol and tannic acid. The indigo-brown, which is soluble in alkalis, is chiefly found in samples in the preparing of which lime has been employed. Berzelius's plan is to first wash the sample to be analysed with hydrochloric or acetic acid, then with alkali, and finally with alcohol and hot water, which will remove the three mentioned bodies, and leave a fairly pure indigo-blue. This contains, however, a certain quantity of silica or other mineral matter, which the acids and alkali have failed to remove. Although the amount of this mineral matter may be estimated by incineration, the author thought better results still might be obtained by estimating the nitrogen in the purified product by Kjeldahl's process and calculating from this the percentage of indigo-blue. For his experiment he used a sample of common Bengalese indigo. The washings with acid, soda, alcohol, and hot water were quickly performed in a perforated crucible, closed with asbestos and connected with a filter-pump. The asbestos containing the indigo-blue was then dried, and finally treated with sulphuric acid and a drop of mercury. The nitrogen multiplied by 9.36 equals the indigo-blue. Pure sublimed indigo-blue showed 99.85 per cent. The common Bengalese sample gave 75.76 per cent.

L. DE. K.

#### VOLUMETRIC ESTIMATION OF PHENOL, THYMOL, NAPHTHOL, AND SALICYLIC ACID.

J. MESSINGER AND G. VORTMANN have found that the principles of the process by which aristol and similar compounds are obtained—viz, treatment with iodine of a strongly alkaline solution of thymol, etc.—may be applied to the quantitative estimation of the above-named substances, and no doubt also of others chemically allied to them.

The requisite volumetric reagents are, a  $\frac{1}{10}$  normal solution of iodine and a  $\frac{1}{10}$  solution of sodium hyposulphite.

In the estimation phenol or carbolic acid, the latter must be in alkaline solution. For each molecule of phenol there will be consumed 6 atoms of iodine. The mode of proceeding is as follows: 2 to 3 grams. of the phenol to be estimated are dissolved in soda so that there are at least 3 molecules of soda present for every molecule of phenol. The



solution is then diluted to 250 or 500 c.c. Of this an exactly measured quantity of 5 or 10 c.c. is put into a small flask, the contents heated to about 60° C., and enough of the  $\frac{1}{10}$  iodine solution added to render the liquid strongly yellow by excess of iodine. Upon agitation a bright-red precipitate will fall. After the liquid has cooled, it is acidulated with dilute sulphuric acid, diluted to 250 or 500 c.c., and a definite portion (say 100 c.c.) titrated with  $\frac{1}{10}$  hyposulphite in order to ascertain the excess of iodine. The actual amount of iodine consumed (in grams.), multiplied by the factor 0.123518, gives the quantity of pure phenol. The factor is derived thus:

$$\frac{1 \text{ mol. phenol}}{6 \text{ at. iodine}} = \frac{93.78}{759.24} = 0.123518$$

The analytical data furnished by the authors show that this method of estimation is very satisfactory, differences not exceeding 1.2 per cent.

Thymol can be similarly determined, but no heat is required. The precipitate caused by iodine has a brownish-red colour. Each molecule of thymol requires 4 atoms of iodine. The amount of iodine actually consumed, multiplied by 0.2956772 indicates the quantity of thymol.

From 0.1 to 0.3 gram. of thymol is dissolved in soda, so that there are at least 4 molecules of soda for 1 of thymol. The solution is then made up to 250 or 500 c.c. and, except that no heat is applied, treated as in the case of phenol.

*Naphthol (beta).*—This yields, under the same conditions, a dirty-green precipitate. Here also 4 molecules of soda must be taken for every 1 molecule of naphthol. The amount of iodine actually consumed must be multiplied by the factor 0.37843106. In the case of naphthol, the solution must be heated to 50° to 60° C. Otherwise the method is the same.

*Salicylic Acid.*—This may be estimated either alone or when mixed with benzoic acid, the latter not entering into reaction. In this case, also, 4 molecules of soda must be taken for every molecule of the acid. On adding the  $\frac{1}{10}$  iodine solution to the solution of the acid warmed to 50° to 60° C., a precipitate should not be formed at once. Only after iodine is present in excess, and the liquid has been again slightly warmed, is there produced a bright-red precipitate, which increases in quantity after acidulation. If too small a quantity of alkali was present, a yellowish-white precipitate is formed before iodine is present in excess. Should this happen, more alkali is added until this precipitate disappears, after which the addition of the iodine solution is continued. The factor with which the quantity of iodine actually consumed must be multiplied is 0.18132606.

The alkali which is used in these processes must be free from nitrite. If not, the latter must be determined separately by means of the  $\frac{1}{10}$  iodine solution, and the proper correction made when the alkali is employed.

Calculations of the results obtained by the above processes may be saved by the following consideration:

Let  $f$  denote the factor with which the quantity of iodine must be multiplied in each case, and  $t$  the titer—that is, quantity of iodine in 1 c.c.—of the iodine solution; then the product  $f \times t$  at once shows the quantity of phenol, etc., in grams., which corresponds to 1 c.c. of the iodine solution.—*Berichte*, 1890, 2753, and *Am. Drug.* xx. 56.

**MICRO-CHEMICAL INVESTIGATION OF EXPECTORATION.** PROF. FERDINAND HUEPPE (*Chemiker-Zeitung*, 17th Dec., 1890). The author uses the following apparatus :—(1) A microscope, which need not as a rule be provided with the strongest powers, then, owing to the staining process, even isolated bacteria are readily recognised. However, it is as well to have a  $\frac{1}{12}$  inch power at command. (2) Some salt-cellars and a few crystallisation basins of about 5-6 C.M. diameter, and a depth of 1 C.M. (3) A small pair of bellows connected with a finely drawn-out glass tube. (4) A pair of pincers and a few platinum needles. These are made by fusing into a glass rod of about 20 C.M. length a 5 C.M. long platinum wire. Either before or after use the points must be ignited, and then just allowed to cool. (5) A spirit lamp or a Bunsen-burner. (6) Test-mixers, burettes or pipettes, and a balance. (7) To get a fair sample of the expectoration the author uses a cylindric glass holding about 100 c.c. provided with a ground stopper. To measure off the fluid a pipette is used, capable of accurately delivering .01 c.c. In using the pipette the top must be closed with a piece of sterilised cotton wool, or what is still better, it should be connected with an aspirator.

**Reagents.**—(1) Recently boiled distilled water, which must be of course perfectly sterilised.

(2). Absolute alcohol or 90 per cent. spirit. These are used for dissolving the colours, also to prepare a 60 per cent. spirit.

(3). A 5 per cent. solution of phenylic acid.

(4). Sulphuric, hydrochloric or nitric acids, diluted with ten times their bulk of water. They are used for the purpose of decolourising.

(5) To stain the bacilli, a solution is used containing 1 per cent. of fuchsine, 10 per cent. of alcohol, and 90 per cent. of the carbolic acid solution. The fuchsine must be first dissolved in the spirit before the carbolic acid is added. The solution keeps for many months.

(6). For the purpose of staining are wanted :—

(a). Watery methylene blue, which means the solution of the dye in water (which must, however, often be filtered or even renewed), or an alcoholic solution is added to water in sufficient quantity immediately before use.

(b). Yellow fluoresceine in a saturated alcoholic solution of methylene blue.

(c). Picrate of aniline. Aniline oil is saturated with powdered picric acid. A few drops of this solution are added to a small cup full of aniline.

The collecting and sending out of the expectoration must be done in thoroughly cleansed glass bottles, provided with ground glass stoppers. The morning product is the best fitted for the experiments, particularly if the patient is improving.

For quantitative estimation it often becomes necessary or desirable to specially prepare the expectoration. A saturated solution of borax is mixed with three parts of water. According to the consistency of the expectoration it is thoroughly shaken in a test-mixer, with an equal or even a treble volume of the borax solution for about a minute, until all coarse lumps have disappeared. The liquid is then put into a conical glass, and after this is covered over, allowed to settle for 24-48 hours. The clear fluid is then poured off, and the deposit used for the experiment. This complicated process

need only be resorted to when the direct testing of the expectoration has given no satisfactory result.

**Preparation of the slides.** When the expectoration is fresh, a little is taken out by means of the platinum needle; not the watery fluid but the pus-like part. If prepared a drop is taken by means of the pipette. The material is spread over the covering glass by means of the platinum needle with the utmost care. The layer need not be particularly thin, but *must* be as much as possible uniform. This may be assisted by the application of a gentle blast of air from the bellows, which will also get rid of the moisture.

**The fixing.** The cover is got hold of with the pincers and passed three times (the material upwards) through the Bunsen flame. The objects are then ready for staining.

**Staining.** The specimens look most beautiful when stained whilst cold. A drop of the fuchsia solution is spread over the cover and allowed to act for five minutes; or the cover is made to float on this fluid, contained in a little dish for the same length of time. The time may be shortened to about one minute if the solution is applied boiling hot. After the staining, we must decide whether other bacilli besides tuberculi-bacilli are to be looked for. Ordinary phthisis is no longer considered to be pure tuberculo-se, but a mixed infection. The methods which enable us to detect the other bacteria as well are not, however, so accurate for the detection of the tuberculi-bacilli as the special methods. It is therefore as well to apply them both in succession.

\* **A.** The operator wants to test for the tuberculi-bacilli only. The excess of colouring matter is carefully removed from the cover by means of blotting-paper, and the glass is then dipped for a few seconds in the dilute mineral acid, until the colour seems all gone. If, however, the layer is somewhat thickish, it is as well not to immerse it too long. The covering glass must now be well washed with water and then quickly dried by means of the bellows.

A drop of the picrate of aniline is now put on a slide and the covering glass put on downwards. The excess of aniline is removed by means of blotting-paper, and the *outside* of the cover is then moistened with a drop of a suitable oil.

The objective is now lowered until it touches the globule of oil, and any experienced microscopist will soon recognise the tuberculi-bacilli, appearing as they do like red rods on a yellowish field. There is little chance of mistaking them for bacteria.

**B.** Testing for tuberculi-bacilli in presence of other bacteria. The colouring by means of fuchsine and the bleaching by acids is just as in A. The acid must, however, only act for a few seconds, when the slide is immediately immersed into 60 p.c. alcohol, contained in two separate basins. After draining off the spirit a drop of the saturated watery solution of methylene blue is put on, but washed off again after one minute.

The cover is now put on a slide with a drop of water. Its outer surface, after being dried with blotting-paper, is moistened with a drop of oil and the microscopical examination is conducted as usual. The tuberculi-bacilli appear red on a blue field, but their number seems to have somewhat diminished. The other bacteria will all be coloured blue.

If one likes to avoid the use of mineral acids (to prevent accidents to the microscope) the following process may be recommended: The staining with fuchsine is done as usual, and the cover is then dipped six or ten times in succession into the fluorescein methylene blue then about ten times in a strong alcoholic solution of methylene blue, and finally washed with water. This will also communicate a red colour to the tuberculi-bacilli, while other bacteria will look blue. L. DE K.

**ELDERBERRY JUICE AS AN INDICATOR.** BY CLAUDE C. HAMILTON, M.D., PH. G.—The expressed juice of the fruit of *Sambucus canadensis*, or elder, has a garnet-red colour when neutral or acid, but turns green when alkaline. This property led to some experiments by the author as to its value as an indicator in volumetric analysis. These experiments show the elderberry juice to be not only superior to litmus for any titrations, but equal in efficiency to rosolic acid as an indicator in the estimation of ammonia or phosphoric acid. When the indicator is first added to ammonia the colour is a "muddy" blue, becoming clearer and of a pea-green colour as the acid is added from the burette. This green is brighter and more distinct as the final end to alkalinity approaches, and, when a drop of acid is added in excess, instantly becomes a garnet-red colour. The turn of the indicator was exactly at the number of cubic centimeters required to turn rosolic acid yellow, while phenolphthalein gradually faded out at a few tenths cubic centimeters more.

In titrating the precipitate of  $MgNH_4PO_4$  by Stolba's method, the red colour appears at just twice the cubic centimeters of HCl required to turn rosolic acid yellow. If the precipitate is dissolved in HCl and the excess measured back by NaHO, the green appears at just twice the cubic centimeters required to turn rosolic acid red. At the point where rosolic acid just turns, elderberry juice has a violet colour. Then when the formula is  $Na_2HPO_4$ , the elderberry juice is green, and is not restored to acid till the formula is  $H_2PO_4$ . The final point is more distinct when the  $MgNH_4PO_4$  is dissolved in excess of HCl and the acid measured back by NaHO. The author is engaged on further experiments in regard to the action of this substance with phosphates to determine its practical value.

In titrating carbonates a bluish-violet appears at the point when phenolphthalein is just decolourised (without heating), and changes to red at the same point that methyl orange is turned red. The change of colour is not very distinct, depending on keeping the solution at a constant temperature. These experiments were made with elderberry wine carefully neutralised with NaHO. The fresh juice may be preserved by addition of one-fifth its volume of alcohol. The author finds it quite efficient in all titrations, unless it be acetic acid, when the colours seem so pale as to be rather indistinct.—*Amer. Drug*, XX., 50.

**A NEW METHOD OF TESTING HONEY.** BY DR. OSCAR HAENLE.—It is only about five years back that every expert would have condemned as adulterated any honey which was found to turn the ray of polarised light to the right instead of the left. About that time Dr. Haenle succeeded in finding, while travelling, some natural (wild) honey which polarised to the right. This was subsequently ascertained to be due to the fact

that the bees fed upon coniferous products, while those feeding upon flowers produced lævogyre honey. While the polariscope had, before this discovery, been generally used as a certain criterion to distinguish between genuine and adulterated honey, this instrument could no longer be employed for the purpose without some restriction. The author has now ascertained that if the honey be dialysed before the polarisation test is applied, the result is a certain indication of the character of the honey.

I. EXPERIMENTS WITH HONEY COLLECTED FROM FLOWERS.—1. A pure Alsatian honey was dissolved in twice its weight of water. The solution polarised  $28^\circ$  to the left ( $-28^\circ$ ). It was then subjected to dialysis during sixteen hours, after which the residue remaining in the dialyser was optically inactive ( $0^\circ$ ).

2. Thirty grams. of a pure honey were dissolved in 150 grams. of water, the solution decolourised and then dialysed. After eighteen hours the residue was inactive.

3. Fifty grams. of a similar honey were dissolved in 250 grams. of water. The solution polarised at  $-11^\circ$ . After sixteen hours' dialysis the residue was optically inactive. On further evaporating the latter and again dialysing, its inactivity remained unaltered.

II. EXPERIMENTS WITH GLUCOSE SYRUP.—A 10 per cent. solution of glucose syrup which polarised  $+100^\circ$ , was decolourised and then dialysed. After sixteen hours it still polarised  $+5^\circ$ . The residue was then concentrated, and in proportion as this progressed so rose the angle of polarisation.

III. EXPERIMENTS WITH HONEY PURPOSELY ADULTERATED.—1. Forty grams. of a pure honey, polarised in a 1 in 2 solution at  $-35^\circ$ , were mixed with 10 grams. of glucose syrup. A 10 per cent. solution of this mixture was subjected to dialysis, and the residue was found to remain dextrogyrate at  $+4^\circ$ .

2. Thirty grams. of a pure honey were mixed with 20 grams. of glucose syrup, dissolved in 250 parts of water, and the solution decolourised by charcoal. It polarised at  $+65^\circ$ . After twenty-four hours' dialysis the residue retained a permanent polarisation of  $+14^\circ$ . After concentrating this residue to half its weight its polarizing angle had increased to  $+60^\circ$ .

3. Fifty grams. of a glucose honey were dissolved in 250 grams. of water. The solution polarised at  $+95^\circ$ . It was then dialysed and the liquid on the dialyser examined at intervals of two hours. The following is the rate at which polarisation decreased until it remained constant :

|               |      |
|---------------|------|
| After 2 hours | +45  |
| " 4 "         | +33  |
| " 6 "         | +18° |
| " 8 "         | +15° |
| " 9 "         | +12° |
| " 10 "        | +11° |
| " 11 "        | +10° |
| " 12 "        | +10° |

Further dialysis did not change the angle ( $+10^\circ$ ).

*General conclusions.*—Any honey which, after having been dialysed, does not turn the ray of polarised light to the right, is free from glucose. Any honey which, after dialysis, retains a permanent dextrogyre polarisation, contains glucose.—*Amer. Drug*

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL meeting of the Society was held on Wednesday, the 1st ult., at Burlington House, the President, Mr. Otto Hehner, in the chair.

The minutes of the previous meeting were read and confirmed.

Mr. R. H. Gerrans, assistant to Mr. Cassal, was proposed as an associate.

The following papers were read and discussed:—

“Some Further Points in the Detection of Adulteration in Vinegar,” by Dr. W. J. Sykes.

“The Detection of Butter Adulterated with Coco-nut Fat,” by Dr. Muter.

“On Measuring Milk for Quantitative Analysis,” by Dr. Vieth.

“Extraction of Fat from Milk Solids,” by A. W. Stokes.

The next meeting will be held at Burlington House on Wednesday, the 6th inst.

## NOTE ON MALT VINEGAR.

BY OTTO HEHNER.

(Read at the Meeting, March, 1891.)

ON several occasions samples of vinegar have been submitted to me with a view to ascertain whether they could be correctly described as malt vinegar. It is well known that much of the vinegar sold is either made from sugar or from a specially prepared pyroligneous acid, such products being coloured with caramel, and possessing, when admixed with some real malt vinegar, to all appearance the properties of genuine malt vinegar. I am not acquainted with any directions to enable the analyst to distinguish these mixtures from the genuine article, and although I cannot pretend to have gone very exhaustively into the matter, the following analyses may yet supply some slight help to other workers in this field.

Vinegar when prepared from malt must contain all soluble mineral constituents of the grain, whilst artificial vinegars are more or less devoid of ash, and almost wholly so of phosphoric acid. The solid matters of dry malt extract contain about from .7 to .8 per cent. of phosphoric acid ( $P_2O_5$ ), and a similar ratio is found in beers made from grain only, calculating in the usual manner the original gravity and the percentage of  $P_2O_5$  upon the original solids. In the case of vinegar the original gravity cannot, as far as I am aware, be calculated with any degree of accuracy on account of the varying loss of alcohol and acetic acid which is almost unavoidable during the process of manufacture. If we add to the total solid matter found in a sample of vinegar the amount of sugar corresponding to the acidity, 120 parts of acetic acid corresponding in theory to 180 parts of glucose, the original solids are certainly underestimated, and the percentage of phosphoric acid calculated upon these, therefore, correspondingly too high. But for the purpose of comparison, such a rough calculation will give sufficiently approximate results, as will be seen from the following figures. Table No. I includes vinegars partly to my knowledge undoubtedly made from malt only, partly made by the best London manufacturers.

TABLE I.

|                                | 1.   | 2.   | 3.   | 4.    | 5.    | 6.   | 7.   |
|--------------------------------|------|------|------|-------|-------|------|------|
| Acidity .. .. .                | 3.07 | 2.88 | 3.70 | 6.48  | 5.73  | 4.16 | 3.79 |
| Total solids .. ..             | 3.26 | 2.72 | 4.01 | 2.44  | 2.46  | 1.68 | 4.23 |
| Ash .. .. .                    | .39  | .41  | .31  | .31   | .47   | .22  | .32  |
| $P_2O_5$ .. .. .               | .13  | .12  | .13  | .088  | .092  | .096 | .067 |
| Alkalinity ( $Na_2CO_3$ ) ..   | .072 | .084 | .037 | .076  | .089  | .017 | .076 |
| Calculated original solids ..  | 7.86 | 7.04 | 9.56 | 12.12 | 11.05 | 7.92 | 9.92 |
| $P_2O_5$ in original solids .. | 1.65 | 1.70 | 1.36 | .73   | .83   | 1.21 | .68  |

Samples 1, 2, and 3 are evidently made at so high a temperature that much loss of alcohol or acid took place, the proportion of phosphoric acid being extraordinarily high.

Table II. contains analyses of samples, some of which were acknowledged to be mixtures, but most having been bought as malt vinegar; obviously none, except samples 8 and 9, were pure malt vinegars:—

|                             | 8.   | 9.    | 10.   | 11.  | 12.  | 13.   | 14.  | 15.   | 16.  |
|-----------------------------|------|-------|-------|------|------|-------|------|-------|------|
| Acidity .. .. .             | 4.44 | 5.16  | 7.52  | 4.56 | 4.70 | 6.00  | 4.44 | 5.20  | 4.79 |
| Total solids .. ..          | 1.23 | 2.30  | .27   | .64  | 1.54 | 2.06  | 2.46 | 3.40  | 1.00 |
| Ash .. .. .                 | —    | —     | .029  | —    | .34  | —     | —    | —     | .16  |
| $P_2O_5$ .. .. .            | .074 | .098  | trace | .013 | .018 | .026  | .026 | .035  | .026 |
| Alkalinity .. .. .          | —    | —     | none  | —    | .045 | —     | —    | —     | .037 |
| Original solids ..          | 7.89 | 10.04 | 11.55 | 7.48 | 8.52 | 11.06 | 9.12 | 11.20 | 8.18 |
| $P_2O_5$ in original solids | .94  | .97   | 0     | .18  | .21  | .23   | .28  | .31   | .32  |

The phosphoric acid in all cases was estimated by the Molybdic method, as described by me in ANALYST, Vol. IV., p. 23.

## DISCUSSION.

Mr. CASSAL said that a limit of 3 per cent. of acetic acid had been fixed for vinegar, and if anything below that amount were found in a sample, a public analyst was justified in certifying to adulteration. He understood that Mr. Hohner did not intend to convey that a watery solution of acetic acid of any strength was vinegar, and that he adhered to the 3 per cent. limit. He desired to ask whether the figures given represented total acidity or acetic acid, and whether Mr. Hohner regarded the sample giving the figure 2.88 as a genuine malt vinegar; also whether the other samples could be

guaranteed as being genuine malt vinegars. He might mention that he had had some official cases of vinegar adulteration. He had taken 3 per cent. of acetic acid as the basis for calculation, which was certainly low enough, and had certified to minimum percentages of extraneous water. In two cases, in each of which he had certified the presence of at least 30 per cent. of water, the reserve samples were sent to the Somerset House chemists, who had confirmed his certificates and had stated the same percentages. Mr. Cassal also wished to ask Mr. Hehner his reasons for calculating the original solids and referring the phosphoric acid to those solids.

Dr. SYKES said that from the manner in which vinegar was manufactured nowadays, *i.e.*, allowing a fermented malt wort to slowly trickle over twigs or shavings impregnated with the acetic ferment, contained in a vessel to which air had very free access, the whole process being conducted at a temperature of 80° to 90° Farht., naturally an enormous loss of alcohol and acetic took place by evaporation; and he thought that this loss would quite account for the large amount of phosphoric acid the President had obtained, very much more malt extract being used up than the acetic acid in the sample would represent. He did not think that sour beer could be used to any extent in vinegar making, since in sour ales there was usually besides the product of the acetic ferment, also the products of a number of unknown ferments, some of which were of an exceedingly nauseous character. He thought the paper a most useful and suggestive one.

#### SOME FURTHER POINTS IN THE DETECTION OF ADULTERATION IN VINEGAR.

By DR. W. J. SYKES, D.P.H., F.C.S.

(*Read at Meeting, April, 1891.*)

IN thinking over our President's paper, read before you last meeting, it occurred to me that the nitrogenous constituents of a vinegar might afford some additional clue as to its genuineness or otherwise. Malt, as you all know, contains a fairly large amount of nitrogenous matter varying under normal conditions from some 8 to 12 per cent. About 45 per cent. of this is soluble in water, and some portion of this ought to be found in the finished vinegar.

Since all calculations made upon the constituents of malt found in a vinegar must necessarily be based on the quantity of malt originally used in the preparation of that vinegar, it becomes necessary to ascertain first of all how close an approximation to this quantity can be found from an examination of the products formed by fermentation. In order to do this I shall have to touch briefly on the subject of vinegar manufacture.

The first step in this process is the preparation of the mash, which is effected by mixing intimately crushed malt and water heated to such a temperature that the resultant mixture has a temperature of 140—145° Farht. The mash is allowed to stand until diastatic action is complete, the whole of the starch of the malt being converted into soluble hydrolysis products, then the liquid portion, *i.e.*, the wort is drained off. The wort, after being sufficiently cooled, is made to undergo the alcoholic fermentation by the addition of beer yeast. Some makers, however, boil their wort first, by this means precipitating the dissolved albumen, and obtaining in this manner a brighter solution. On the other hand those makers who ferment the wort unboiled save the expense of firing, and no doubt secure a better yield of alcohol. It has been shown by



Mr. H. Brown and Dr. H. Morris that in the process of mashing there are formed besides dextrin and maltose, a number of intermediary compounds of these two bodies, which have been named amyloïns. It is supposed there are some eighteen of these bodies, beginning with one molecule maltose nineteen dextrin, two molecules maltose eighteen dextrin, and so on until nineteen maltose and one dextrin is arrived at.

The members of this group which contain most dextrin are said to be unfermentable by the *Saccharomyces Cerevisiae*, but can be completely broken down by diastase to fermentable maltose; consequently the manufacturer who ferments his wort unboiled leaves his diastase intact, and this gradually converts the amyloïns into a sugar capable of being fermented completely away.

The alcoholic wort, freed as much as possible from yeast, is now subjected to the action of the acetifier. This is a vessel with a false bottom perforated with numerous fine holes situated some inches above the real bottom. A few inches from the top of the vessel, what may be called a "head," perforated with very fine holes, is fixed. The intervening space between the head and the false bottom is filled with twigs or wood shavings impregnated with the acetic ferment. The alcoholic wort is placed in the space above the head, and passing through the fine holes in it, slowly trickles over the acetifying material. Free aeration is obtained by a number of holes bored all round the vessel immediately below the head, and also immediately above the false bottom. The partly acetified wort collects in the lower part of the vessel below the false bottom, from which it is returned to the upper portion of the vessel, and thus made to traverse the acetifying material again and again, until acetification is complete. The process is carried on at a temperature of 80° Farht. This free aeration and high temperature naturally leads to much loss of alcohol and acetic acid, and all sorts of schemes have been and are being tried to reduce this loss.

It is found in practice that a wort of 1055 specific gravity yields upon fermentation about 7 per cent. of alcohol; this upon acetification should yield theoretically 9.1 per cent. of acetic acid. But, working under the most favourable circumstances, it is never found to yield more than 6 per cent., consequently a loss of over 34 per cent. takes place. If the process is carried on in a less efficient manner, the loss is considerably higher, the yield not unfrequently amounting to but 50 per cent. of the theoretical one. Since ten parts of malt mashed in one hundred parts of water give a wort of a gravity of 1025—27; taking the lowest of these figures, 22 per cent. of malt would give a wort of 1055 specific gravity; and as this, if worked under the best conditions, produces a vinegar containing 6 per cent. acetic acid, in this case one part of acid would correspond to 3.7 parts malt. Under less favourable conditions of working it might represent 4.9 parts malt. Therefore we cannot go far wrong in assuming that at least 3.7 per cent. of malt has been used for every per cent. of acetic acid found in a vinegar.

The nature of the nitrogenous constituents of malt now claim a brief notice. The grain of barley consists of two portions, the endosperm or reservoir of reserve materials from which the young plant contained in the exosperm is to derive its supply of nutriment, until able to derive its nourishment from the inorganic constituents of the air and soil. The starchy and albuminous matters are present in the endosperm for the most part in an insoluble condition, and before they can be of use for the nourishment of the

young plant, must not only be dissolved but converted into a form capable of passing by diffusion through the walls of its cells. For this purpose certain enzymes or ferments are present, which apparently act in a manner extremely analogous to that in which the animal digestive ferments act. Thus diastase acts upon the starchy portion in the same manner as the ptyalin of the saliva, converting it into maltose and dextrin. A similar digestive process apparently takes place with the nitrogenous bodies, but so far the ferments causing these changes have not yet been isolated. Much work has lately been done in the examination of the action of the digestive ferments upon animal albuminous matter, and this points very strongly to the fact that the digestion of albuminous matter is a process of hydrolysis, treatment with the mineral acids, caustic alkalies and steam under pressure yielding the same products as digestion by ferments. If a mass of coagulated egg albumen be placed in a large quantity of a solution of pepsin acidulated with hydrochloric acid to the extent of 0.2 per cent., and the whole kept at 100 per cent. Fahrht., in a very short time the whole will be dissolved. If at this point a portion of the solution be neutralised nearly the whole bulk of the albumen will come down, and on further addition of alkali it will dissolve; the albumen has been changed into acid-albumen or syntonin, and is now insoluble in a neutral solution as the original albumen was. If in the original solution digestion be carried on for a period of twenty-four to forty-eight hours and a portion be neutralised as before, only a small precipitate will appear, and on boiling no further precipitation occurs. If, however, the solution be saturated with ammonium sulphate nearly the whole of the albuminous matter will come down; it has undergone a further change, and is now in the condition of albumose. On carrying on digestion for a considerable longer time—several days—a stage is reached when the saturation of the solution with  $(\text{NH})_2\text{SO}_4$  no longer causes precipitation. The albuminous matter is now capable of diffusing (though slowly) through a cell wall; it is in the form of real peptone. This seems as far as the ferment pepsin will take a solution of albumen, more powerful hydrolysts, such as caustic alkalies and mineral acids, carry on the process still further, a number of amide bodies being first produced, and further on the whole albuminous matter being broken up into far simpler forms, such as ammonia, carbonic anhydride, urea, etc. If a solution of peptone be made strongly alkaline by caustic soda or potash, and a few drops of an exceedingly dilute solution of copper sulphate be added, a beautiful rose-red colour is produced; this is the well-known biuret reaction which has been considered until lately as characteristic of peptone. It is found, however, to be given by both albumen and albumose, in a somewhat modified form, the colour inclining to violet. Several inorganic compounds also form excellent tests for the various digestion products of albumen, thus potassium ferrocyanide and acetic acid, potassio-mercuric iodide in slightly acetic acid solution precipitate albumen and albumoses but not peptone. Phospho-tungstic acid in strongly hydrochloric acid solution, potassio-bismuthic iodide in slightly HCl solution, and tannin precipitate the whole of the three groups; an excess of tannin, however, redissolves the tanno-peptone precipitate.

The process of malting consists essentially in arousing the dormant vital powers of the barley corn into activity and then again arresting them. One of the first forms of activity displays itself in the secretion of various enzymes or ferments; the first action

being to dissolve the cellulose of the cells containing the starch, the starch itself is also altered to some extent in the direction of soluble starch. Considerable action takes place with regard to the nitrogenous constituents, about twice as much of these are soluble in malt as were soluble in the original barley. The grouping is also different, of one hundred parts of nitrogenous matter in barley sixty-three parts belong to the albumen group, and thirty-seven parts to the amide; in one hundred parts malt forty-six parts belong to the albuminous group, fifty-four parts to the amide. It must be noted that hydrolytic action goes further here than in animal digestion, albuminous matter being evidently converted into the amide form with great ease. The amides being crystalline bodies naturally possess a much higher rate of diffusion than peptones, and are thus able to move about the grain more freely.

If a quantity of malt be mashed in the ordinary manner, the wort filtered off and then boiled, the bulk of the albumen precipitates by coagulation; if the clear filtrate be saturated after cooling with ammonium sulphate, an abundant precipitate forms. This precipitate, which, so far as I know, has never been described before, coming down as it does under the same conditions that the albumoses do in the animal digestion, I propose to call by the same name. If the filtrate from these be diluted with an equal bulk of water, and a small quantity of Alumen's tannin solution\* added, after standing twenty-four hours a very small precipitate of peptone will be observed. Real peptone occurs in malt only in very small traces. The albumoses can be easily estimated by washing with saturated ammonium sulphate solution, the precipitate obtained by saturating a solution with the same salt, drying on a tared filter, and afterwards estimating the ammonium sulphate clinging to the precipitate and filter. The albumoses are not diffusible, and are incapable of nourishing the yeast cell; this I have ascertained experimentally; yeast will not increase in a solution of dextrose with the proper mineral constituents if albumose be the only nitrogenous compound present. They therefore appear in the wort after it has undergone the alcoholic fermentation, and also in the finished vinegar, the bacteria of acetification not completely removing them. Consequently a vinegar prepared from malt always gives a precipitate on saturation with ammonium sulphate; also on the addition of phospho-tungstic acid, or of bismuthopotassic iodide, or mercurio-potassic iodide, and with tannin.

The amide constituents are undoubtedly the ones which supply the yeast and bacteria with nitrogenous food, and are consequently seriously diminished in quantity.

Besides the nitrogenous groups already mentioned, there is still another one present in malt—the gluten group consisting of three members, gluten-casein, gluten-fibrin, and mucedin. All these are more or less soluble in dilute alcohol, and in slightly alkaline or acid solutions. Since all malt worts contain more or less lactic acid, a certain portion of these bodies must go into solution. By long continued boiling they are converted into a coagulated insoluble form. In their chemical reactions they closely resemble the albumoses.

Vinegar, after complete acetification, is heated in order to sterilise; at the same

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\* This exceedingly delicate test for peptone is prepared by dissolving 4 grams. of tannin in 190 c.c. of 50 per cent. alcohol with the addition of 8 c.c. of 25 per cent. acetic acid. One part of peptone in 100,000 pts. of solution gives a perceptible turbidity, and a precipitate after standing twenty-four hours. Excess of precipitant must be avoided.

time certain salts more soluble in hot solution than cold are added. These re-precipitate in the course of twelve or fourteen days, carrying down with them the suspended impurities and a portion of nitrogenous matter; in fact these salts act as a sort of mineral finings.

In estimating the mineral constituents of a vinegar it must be borne in mind that lime salts are often added to the water employed in mashing to secure a more brilliant wort. Also that various kinds of yeast foods containing large amounts of phosphates are often added to the wort with a view to stimulate yeast production and secure a higher production of alcohol.

Various malt substitutes are also frequently employed in vinegar manufacture, such as unmalted barley; a number of gelatinised preparations are also in the market made from rice and maize; the use of all these would slightly lower the percentage of soluble nitrogenous matter in the wort and finished vinegar. Sugar is also employed, and if used in any quantity would seriously lessen the quality of nitrogen found in the vinegar.

I found in a vinegar which I had every reason to suppose genuine 6.5 per cent. of acetic acid; this figure multiplied by 3.7 would give 24.05 per cent. malt originally used. Assuming the malt contained 10 per cent. (the average amount) of soluble nitrogenous matter, of which on an average 45 per cent. is soluble, the wort would have contained 1.08 per cent. soluble nitrogenous matter. The vinegar contained 0.49 per cent. nitrogenous matter, consequently the wort had lost rather less than one half during the processes of conversion into vinegar. The albumoses amounted to 0.213 per cent. It gave an abundant preprecipitate with all the before mentioned reagents.

From this it follows, I think, that considerable information may be gathered from an examination of the nitrogenous constituents of a vinegar as to whether it is genuine or not; but the fixing of limits must naturally be reserved until a long series of experiments have been performed in this particular direction.

In conclusion, I beg to acknowledge my indebtedness to a series of papers by Mr. J. A. Nettleton, F.C.S., now appearing in the *Brewers' Journal* on the manufacture of vinegar.

#### DISCUSSION.

The PRESIDENT said that, in his opinion, the custom to lump certain constituents of allied composition together had had a retarding influence upon the progress of our knowledge of food. It was convenient, but unscientific, to calculate, for instance, from the nitrogen the amount of nitrogenous matter, without stating what nitrogenous matters were present, and in what proportions. Such calculation was even frequently very inaccurate, as had been shown, among others, by the late Mr. Wigner in his researches on the nitrogenous constituents of wheat and cocoa. He (Mr. Hehner) was therefore grateful to Dr. Sykes for attempting a discrimination of the albuminoids in the present instance, and for the summary of methods applicable to this object. He hoped that ultimately we would obtain a thorough differentiation of these substances in all articles of food.

Professor WYNTER BLYTH said that 75 per cent. of Dr. Sykes's paper could be found in any chemical primer, but the remaining portion was interesting and important, for there Dr. Sykes showed that the nitrogenous constituents of vinegar could be divided into groups. It was, however, to be regretted a more extensive series of

experiments had not been made, so as to determine the quantity of each nitrogenous group in genuine and spurious vinegars. It would seem that in only one case had this been done. In making a similar investigation on organic fluids, he had found Kjeldahl's process peculiarly applicable, for total nitrogen in the whole could be determined, and then precipitants, like phospho-tungstic acid, could be applied, and the nitrogen in the filtrate determined by Kjeldahl and subtracted from the total nitrogen, thus giving the nitrogen in the precipitate. He had long held the opinion that the only possible way to accurately determine food values was to pass that food through the human intestine in the simplest form, and first to analyse that which goes in (income) and then that which goes out (output). That had been done in a few instances only, but it was the only scientific method of arriving at the value of a food.

Dr. SYKES, in reply, said that the reason he had introduced the subject of animal digestion into the paper was to illustrate the similarity between it and the action of the enzymes upon the proteid matters in germinating barley. With reference to the various reagents he had mentioned, he did not think they were so universally known as Mr. Blyth had suggested. As to the method of estimating the various proteid precipitates by the Kjeldahl process, he had employed this method for some time past. In order to obviate the frequent breakages which occurred in distilling off the ammonia in Kjeldahl's process, where the liquid contained tungstic acid in suspension, he made use of a tin flask, which answered the purpose perfectly.

#### THE DETECTION OF BUTTER ADULTERATED WITH COCO-NUT FAT.

By DR. JOHN MUTER, F.R.S.E., F.I.C.

(*Read at Meeting, April, 1891.*)

THE ever increasing tendency to scientific adulteration teaches us the necessity of not judging the purity of butter by any single one of the accepted tests.

Until some time ago the Reichert process, or one of its modifications, was considered sufficient for all ordinary purposes; and still more recently the use of the oleorefractometer has been declared to be all that is necessary. Now, however, we have the advent of an inventor who is able to take away all taste and odour from coco-nut fat, and thus to render it available as an adulterant where there is a quick sale. To a certain extent it may be used to defeat the "Reichert," because, taking an average good butter, the distillate from which will absorb 14.0 c.c. of decinormal soda, and an average sample of coco-nut fat which will yield a distillate consuming 3.5 c.c., we notice that each 5 per cent. of the latter fat added to butter will only reduce the soda used by about .50 c.c., and it is thus possible to adulterate to the extent of 20 per cent., and yet the butter will pass the 12 c.c. limit; while, if we are to take account of the famous Danish butter and those exceptional samples brought to our notice by Dr. Vieth, we could have a 40 per cent. adulteration passing with impunity by the Reichert process. This is bad, but the refractometer is in a similar position, because if we take one-half coco fat and one-half margarine, we can make an article that shows a refraction of  $-33$ , and thus comes out pure butter. I had, in common with our President, been struck with the fact that there was so much cheap butter about that just showed exactly 12 c.c. with Reichert, and I set myself to solve the mystery, because the use of the small quantity of ordinary margarine necessary to make this reduction would scarcely repay the labour of the manufacture. After some

research I came across several samples absorbing 12 c.c. of soda, and which when examined in the refractometer came out far too good, and I then saw that the key to the whole affair was that the use of coco-fat by the adulterator must be met by the joint employment of both the refractometer and the Reichert on every sample. Given the use by the analyst of both these tests, then the mixing of butter with 25 per cent. of coco-fat, and its passing us as standard butter, will be a thing of the past. In illustration of this I give a few figures of some mixtures that were made with care, and the analysis divided between two persons who did not know what the samples were. The "Reichert" process was done by Mr. Burford, of Leicester, one of my pupils, who is now working on to get his Institute diploma, while the refractions were done by myself.

|               | Nature of Sample.                 | Reichert. | Refraction. |
|---------------|-----------------------------------|-----------|-------------|
| Experiment 1. | All coco-nut fat .. ..            | 3.5 c.c.  | —54         |
| "             | 2. Pure butter of good quality .. | 14.5 c.c. | —34         |
| "             | 3. Butter with 75 per cent. coco  | 6.0       | —49         |
| "             | 4. " 50 " "                       | 9.0       | —44         |
| "             | 5. " 25 " "                       | 12.0      | —39         |

The refraction of the coco-nut fat is so great as to be beyond the scale of the ordinary instrument, and has therefore to be got by using a half-and-half mixture with "typical oil," which shows — 27.

|               | Nature of Sample.   | Reichert. | Refraction. |
|---------------|---|-----------|-------------|
| Experiment 6. | Margarine .. ..   | 1.3 c.c.  | —8.5        |
| "             | 7. Butter with 75 per cent. margarine                                     | 4.5 c.c.  | —15.0       |
| "             | 8. " 50 " "   | 7.8 c.c.  | —22.0       |
| "             | 9. " 25 " "   | 10.9 c.c. | —27.0       |
| "             | 10. Margarine with 50 per cent. coco ..                                   | 2.8 c.c.  | —32.0       |
| "             | 11. Butter with 25 per cent. margarine<br>and 25 per cent. coco-nut fat } | 8.8 c.c.  | —33         |
| "             | 12. Butter with 50 per cent. margarine<br>and 25 per cent. coco-nut fat } | 5.6 c.c.  | —27         |

The margarine used was that now commonly sold in London, and contained some vegetable oil, probably cotton, thus lessening its refraction, that of pure beef oleo-margarine being generally — 13°.

It is thus evident that while each 5 per cent. of coco-nut fat added to butter *increases* its left-handed refraction by one degree, while it *reduces* the soda consumed in the Reichert process by 50 per cent. If, therefore, I had a butter showing a refraction of 37 and a Reichert of 12, I should have no hesitation in charging it with 20 per cent. of coco-fat.

Mixtures Nos. 5 and 9 would pass by a Reichert limit taken on the lowest recorded natural butter, but they are caught by the refraction; while Nos. 10 and 11, which would defeat the refractometer, are at once detected by Reichert.

There is a decided relation between the refraction and the Reichert indication of all pure butters. The highest refraction I ever met with was in a butter showing — 36. I naturally suspected coco-fat, but on applying Reichert I got the large result of 16 c.c. I am now engaged in verifying this relationship, and I put forward the following figures tentatively as a basis for others to take up the matter.

| Refraction. | Reichert. |
|-------------|-----------|
| —36         | 16        |
| —35         | 15.25     |
| —34         | 14.50     |
| —33         | 13.75     |
| —32         | 13.00     |
| —31         | 12.25     |
| —30         | 11.50     |
| —29         | 10.75     |

When we have to deal with butter reduced by margarine this steady relation fails, and we have (as in experiment 9) a drop in the refraction. This matter I put forward tentatively only at the moment, in the hope that it will work out to a useful indication.

### MEASURING MILK FOR QUANTITATIVE DETERMINATIONS.

By DR. P. VIETH.

(Read at Meeting, April, 1891.)

If the first consideration of the analytical chemist in executing his practical work always must be to arrive at reliable and correct results, there is no reason why the second consideration should not be to obtain these results in the most convenient manner.

I have, for years, been in the habit of measuring by means of specially gauged pipettes the quantities of milk required for the determination of total solids, ash, and fat. That it requires less time and is less troublesome to pipette 5 grams. of milk, than to weigh a corresponding quantity, nobody will deny, and I have adopted and adhered to the more convenient way of measuring after having satisfied myself that with ordinary care no inaccuracies occur which could not be safely neglected. When a short time ago, on my mentioning the subject in this room, doubts were expressed whether measuring milk for quantitative determinations was admissible, I resolved to make a systematic series of experiments. The figures, which, with your permission, I am going to submit to you are the results of the investigation.

On the day on which the experiments were carried out the lowest specific gravity observed in any of the milk samples at hand was 1.0315, and the highest 1.0330. These two samples were used, as was also a third sample, representing the mixed yield of a number of dairies, and exhibiting a specific gravity of 1.0325. The temperature of the three samples was brought successively to 48, 60, and 75°F., and quantities were pipetted off and weighed, a pipette being used which was supposed to deliver 5 grams. of milk of the average specific gravity of 1.032 at a medium temperature of 60°F. The weights of the measured quantities were as follows:—

| Sample.                  | I.     | II.    | III.   |
|--------------------------|--------|--------|--------|
| Specific gravity .. .. . | 1.0315 | 1.0325 | 1.0330 |
| Temp. 48°F. .. .. .      | 4.987* | 5.003  | 5.002  |
|                          | 4.998  | 5.001  | 5.003  |
|                          | 4.997  | 5.001  | 5.002  |
| Temp. 60°F. .. .. .      | 4.993  | 5.001  | 5.001  |
|                          | 4.993  | 5.001  | 5.002  |
|                          | 4.994  | 5.002  | 5.001  |
| Temp. 75°F. .. .. .      | 4.990  | 4.991  | 5.001  |
|                          | 4.993  | 4.985* | 4.997  |
|                          | 4.990  | 4.990  | 4.998  |

That specific gravity and temperature are not without some influence is clearly proved by these figures, which show that influence in the direction in which one would expect to find it, the smallest weight of milk being obtained when the specific gravity was lowest and the temperature highest, and the largest weight when the specific gravity was highest and the temperature lowest. As a rule the three quantities measured under equal conditions agree very well; there are, however, two exceptions—they are marked with asterisks—representing the inaccuracies which, perhaps, cannot be entirely avoided when working with pipettes.

Of the twenty-seven quantities measured the smallest weighed 4.985, and the largest 5.003. If we take these two extremes and suppose that we were dealing with a milk containing 11.50 per cent. total solids and 3.00 per cent. fat, instead of these percentages we would find in the one case 11.47 and 2.99, and in the other 11.51 and 3.00. Working upon a milk with 14.00 per cent. total solids and 5.00 per cent. fat, the results would be 13.96 and 4.99 in one instance, and 14.01 and 5.00 in the other. The conditions under which the above samples were taken are about as different as one would ever expect them to be, and the influence of the inaccuracies introduced by measuring the quantities required for the determinations is so small that, I think you will agree with me, it may be disregarded.

If that is so in the case of normal milk samples, the question still remains open what the results would be when one has to deal with abnormal samples. The further experiments were made with a view to answer this question; the various samples were kept at the temperature of 60°F.

I took a skim milk of specific gravity 1.0360. Three quantities measured off weighed 5.038, 5.043, and 5.040. Taking the highest weight, viz., 5.043, and supposing the sample to contain 9.60 per cent. total solids and .40 per cent. fat, the results found would be 9.68 and .40.

I next mixed two parts of milk with one part of water; three measured quantities weighed 4.955, 4.961, and 4.960. Supposing the mixture to contain 8.60 per cent. total solids and 2.60 per cent. fat, the result by taking the smallest quantity of 4.955 would be 8.52 and 2.58.

Of a mixture of two parts of milk and one part of a thin cream the pipetted quantities weighed 4.943, 4.946, and 4.945. I did not analyse the mixture, but it must have contained as near as possible 19.00 per cent. total solids and 10.50 per cent. fat. Using 4.943 grams. for the quantitative determinations, 18.78 and 10.38 per cent. respectively would be found. In this instance, then, we have a difference which cannot very well be neglected.

Lastly, I took a square-shaped six-ounce medicine bottle, put five ounces of milk in, and shook it well each time immediately before drawing off the quantities to be weighed. Pushing the pipette right down to the bottom I obtained 5.012 and 5.008. The stem of the pipette was, of course, wetted with milk outside to a length of about five inches. By repeating the experiment with the only alteration that I wiped the pipette after withdrawal from the bottle, the quantities were 4.990 and 4.981. Pushing the pipette half way down, the quantities weighed 4.980 and 4.979; and taking the samples from one-half inch below the surface 4.971 and 4.969 grams. were obtained.



These latter quantities were increased by leaving the bottle undisturbed for one and a-half minute to 4.985, for three and a-half minutes to 4.991, and for five minutes to 4.999.

Although there is nothing in these experiments which everyone of you could not try for himself any day he liked, I thought it not out of place to put the figures before you, well knowing from personal experience that one does not always find leisure for and pleasure in clearing up even very simple questions.

### FAT EXTRACTION FROM MILK-SOLIDS.

By ALFRED W. STOKES, F.I.C.

*Read at Meeting, April, 1891.*

Though fat can be the most readily and accurately extracted from milk in its liquid form in the manner pointed out by Dr. Hill in the last number of the ANALYST, yet occasionally it may be necessary to determine the fat on the dried milk residue. It may happen that after putting on a portion of the milk for total-solids the rest may be spilt, or the original quantity may be exceedingly small. In such cases both the total-solids and the fat may be separately and accurately determined on only 5 grammes of the milk thus:—

First, dry to constant weight 5 grammes of the milk in a platinum, porcelain, or glass dish, and weigh as usual for total-solids. Now moisten the milk-solids with from 5 to 8 c.c. of strong HCl, cover the dish with a cover-glass, and leave it on the water-bath for from three to five minutes. With a rubber-covered glass rod well break up the contents of the dish. Wash this with hot water into one of the tubes Messrs. Townson and Mercer make for me for the Schmid process (the shorter or old form.) Fill with water to the 20 c.c. mark. Cool. Wash the dish out with ether into the tube, and fill this up to the 50 c.c. mark with ether. Cork the tube. Shake vigorously three times at intervals of three to five minutes. Then let settle, pipette off 20 c.c. of the ethereal solution into a weighed dish. Evaporate off the ether from this, and weigh the residual fat. Lastly note the quantity of ethereal solution left in the tube, and calculate accordingly.

Much more fluffy material marks the junction of the ethereal solution and the dark brown acid liquid than in the ordinary Schmid method. But this material is more apparent than real; it is usually correct to allow only 0.5 c.c. for this, however bulky it may be. There is not the least difficulty in pipetting off the ethereal solution. Even in summer it is only necessary to hold the tube for half a minute under the tap to cool it, and then the ether can be dealt with as leisurely and accurately as so much water.

Swinging the tube round at arm's length will more rapidly separate the ether from the acid liquid.

The method otherwise is such as is detailed in *Chemical News*, of November 1st, 1889. The results obtained are evidenced in the following list of the *whole* of the samples thus analysed during the last twenty-one days. In some cases the fats were also determined by the Schmid method on the liquid milk. The results agreed. For comparison I give the results calculated from total-solids and specific gravity using the admirable table of Messrs. Hehner and Richmond (ANALYST, Vol. xiii. p. 26.) The sp. grs. were taken by the Westphal balance, and the total-solids were dried to constant

weight. I append the total-solids merely to show the sort of milks dealt with, they were not specially prepared, but were received in the ordinary course of work.

I have arranged them in the order of quantity of fat, showing that the method works as well with poor as with rich milks.

| Total Solids. | Fat Found. | Fat Calculated. |
|---------------|------------|-----------------|
| 6.28          | 1.46       | 1.47            |
| 10.91         | 2.56       | 2.60            |
| 10.12         | 2.79       | 2.80            |
| 11.06         | 2.80       | 2.74            |
| 9.90          | 2.84       | 2.85            |
| 10.78         | 2.84       | 2.89            |
| 11.90         | 2.97       | 2.98            |
| 10.95         | 3.03       | 2.97            |
| 11.63         | 3.28       | 3.23            |
| 11.97         | 3.57       | 3.51            |
| 12.89         | 3.84       | 3.87            |
| 12.56         | 3.87       | 3.89            |

Here, the differences between fat found and calculated range from +.05 to —.06, the average being .02.

A sample of stale milk twenty-one days old gave by this method 3.09 fat, and by Schmid method on the stale but liquid milk 3.01.

Here the main difficulty is in taking a correct sample, hence the larger difference. Some of these results were obtained by my assistant, Mr. W. N. Yarrow, to whose careful work I am greatly indebted, and some by myself.

Mr. A. H. Allen's suggestion to pipette off as much ether as possible, then to shake with some more ether, and add this to the former quantity would, I think, obviate the difficulty found at times of reading off the quantity of ether left in the tube. But it would also about double the time taken by the whole operation. By an apparatus I am now constructing I think it will be possible to take the specific gravity on 5 c.c. of milk. So that accurate determinations of total solids, fat and specific gravity may all be made on the same 5 c.c. of milk, if necessary.

*(Conclusion of the Society's Proceedings.)*

#### TESTING OF COMMERCIAL TOLUIDINE.\*

By F. F. RAABE.

EVEN in the aniline trade the necessity has been felt of late years to sell pure products with guaranteed analysis, particularly in the case of aniline and toluidine. At one time most of the toluidine offered for sale was tested by the buyers as to its specific gravity and boiling point, but now they demand a specified percentage of *p* toluidine. The estimation of this body in presence of *o* toluidine and aniline often leads to disputes with the manufacturers, because the testing is not always done precisely in the same manner.

The aniline works which obtain their benzol, 50-90 per cent., from England, know that they must exactly stick to the specification or contract. This provides for the size of the retorts, length of the condenser, distance of thermometer from bottom of retort, etc., etc., in order to get concordant results. To prevent as much as possible analytical differences in the testing of toluidine, it is absolutely necessary for the buyers to agree with the manufacturers on a definite method of testing. As I have lately been often consulted as to a reliable process for the estimation of *p* toluidine, I will now communicate the various methods from time to time proposed. In testing toluidine, one must take particular notice of its appearance, which should be as clear as a brewer likes to see his ale. The colour may, however, be spoiled to some extent when the sample has been stored in iron barrels. To ascertain the boiling point, and consequently the presence of higher homologues, 100 c.c. of the oil are fractioned in a retort holding about 180° C., the heat being so regulated that about two drops distil over every second. The specific gravity is taken with the bottle, or also very accurately with a large hydrometer, by preference the one devised by Lunge. To get the temperature exactly at 15° C., the oil is put into a cylinder, which is then put into a second cylinder, filled either with warm or, if necessary, iced water.

For the estimation of *p* toluidine many processes have been proposed, and the method to be chosen ought to be such a one as can be readily mastered by the most inexperienced who works on not too small quantities of the sample. Merz and Weith take advantage of the little solubility of *p* toluidine in water, which process was further worked out by Schoop. Rosenstiehl noticed the little solubility of *p* toluidine oxalate in ether, which process was simplified by Nietzki, and particularly by Lorenz. Lunge recommends the taking of the specific gravity, and has published an excellent table; whilst Schön treats the sample with potassium dichromate and hydrochloric acid, and then tests colorimetrically. I have tried a totally new idea, which consisted in dissolving pure *p* toluidine in the sample and ascertaining the solidifying point of the mixture. I cannot recommend the colorimetric process, as this is too much influenced by the personal equation in working.

The specific gravity process is very much influenced by slight alterations in temperature, and also by the presence of small quantities of aniline. Schoop's acetyl process may be used when the sample is of at least 30 per cent. strength, by operating as follows:—The toluidine must have been dried with calcium chloride or potassium carbonate. Ten grams. of the sample are boiled, under a reflux condenser, with 10 c.c. of acetic anhydride. After cooling, 30 c.c. of glacial acetic acid are added, and the mixture poured into 400 c.c. of hot water, the flask being rinsed with another 200 c.c. of water. The liquid is then kept for twenty-four hours at a temperature of 0° C., which causes the separation of acetotoluidine, which may be collected on a weighed filter, slightly washed with dilute acetic acid, dried first by pressure between blotting paper, and finally at a temperature of 98° C. 149 parts of the precipitate correspond with 107 parts of *p* toluidine.

The oxalate process is most conveniently performed according to Lorenz's directions. If applied in an empirical sort of way, the results are very good. What is wanted is pure ether, free from alcohol and water; a solution of 1.062 grams. of dry oxalic acid in

250 c.c. of ether; deci-normal solution of carbonate of soda; pure *o* and *p* toluidine, and also very delicate litmus paper. First of all, 10 c.c. of the ethereal oxalic acid solution are put into a flask containing 25 c.c. of water, and, after removing the ether by distillation, the residue is titrated with the sodium carbonate, litmus paper serving as indicator. Two grams. of pure *p* toluidine are now dissolved in 70 c.c. of ether, with two drops of *o* toluidine and so much of the oxalic acid solution added until all the *p* toluidine is precipitated, which may be easily recognised by the turning red of litmus paper. After adding another 2 c.c. of the acid, the whole is allowed to stand for four hours at a temperature of 15° C., when the precipitated oxalate is filtered off and washed with about 30 c.c. of ether, both filtrate and washings being collected in a flask containing 25 c.c. of water. The ether is distilled off, and the residue again titrated with the soda, when the difference between the two titrations will give us the check on the oxalic acid, which may then be used to test the commercial sample. I have tried to use a watery solution instead of the ethereal one, and have obtained very satisfactory results when analysing samples containing from 25-40 per cent. of toluidine. The acid must, however, be added in large excess, and the precipitate weighed. After a few more experiments, I hope to say something more on the subject. The solidifying or crystallisation process is, however, a much quicker one. When the sample is fused with from 1-3 parts of pure toluidine, a mixture is obtained which may be tested by taking its solidifying point. With the same weight of pure *p* toluidine, the percentage of the mixture is got accurate within .5 per cent., with double the weight .33 per cent., with treble the weight .25 per cent. For instance:—

|                              |          |   |                  |   |                 |           | Difference. |
|------------------------------|----------|---|------------------|---|-----------------|-----------|-------------|
| 10 Toluidine of 50 per cent. | <i>p</i> | + | 10 pure <i>p</i> | = | 20 Toluidine 75 | per cent. | .5          |
| 10 "                         | 50 "     | + | 10 "             | = | 20 "            | 75.5 "    |             |
| 10 "                         | 30 "     | + | 20 "             | = | 30 "            | 76.66 "   | .33         |
| 10 "                         | 31 "     | + | 20 "             | = | 30 "            | 77 "      |             |
| 10 "                         | 30 "     | + | 30 "             | = | 40 "            | 82.5 "    | .25         |
| 10 "                         | 31 "     | + | 30 "             | = | 40 "            | 82.75 "   | —           |

A 30 C.M. thermometer, running from 30-50° C. and graduated in  $\frac{1}{2}^{\circ}$ , shows a difference of .2 per cent. of paratoluidine. The process is, therefore, very suitable for being daily used by manufacturers.

It is as well to have at hand a number of standard samples, containing, say, 82.5, 83, 83.5, 84, 84.5, and 85 per cent. of *p* toluidine, to be compared with any given sample. I will later on communicate in how far the crystallisation point is influenced by the presence of any moisture.

## THE ELECTROLYSIS OF METALLIC PHOSPHATES IN ACID SOLUTION.

By EDGAR F. SMITH.\*

In a former article, bearing the above title, I showed that copper and cadmium could be precipitated electrolytically from solutions of their phosphates. Their separation from each other was also noted, as well as the separation of the individual metals from iron, aluminium, chromium, zinc, nickel, and cobalt. Further, the separation of copper from manganese was shown to answer all practical requirements. The free phosphoric acid, present in the solution, prevented the deposition of the manganese as dioxide.

\* *American Chemical Journal.*

Since reporting this last separation I have found that cadmium can be separated from manganese electrolytically without any particular difficulty.

*Cadmium from Manganese.*

When I electrolysed the acid phosphates of copper and manganese, 10 c.c. of phosphoric acid (sp. gr., 1.347) were present in the solution. The current employed gave 0.10 c.c. OH gas per minute. In the presence of such a large excess of acid, cadmium was not precipitated by a current yielding 10 c.c. OH gas per minute. It therefore became necessary to know just what quantity of free acid could be present in the solution and the cadmium be entirely deposited. The quantity of acid requisite for the retention of the manganese was of importance. Several trials led to the following conditions as being best suited for the complete separation of the metals under discussion :

1. 10 c.c. cadmium sulphate solution (= 0.2399 gram. cadmium), 10 c.c. manganese sulphate solution (= 0.1000 gram. manganese), 20 c.c. disodium phosphate (sp. gr., 1.0358), 3 c.c. phosphoric acid (sp. gr., 1.347), and 100 c.c. water were electrolysed with a current liberating 10 c.c. OH gas per minute. In twelve hours 0.2394 gram. cadmium was precipitated. Not the slightest deposition of manganese dioxide was observed upon the anode.

2. In this trial the conditions were precisely the same as those given in 1. The deposit of cadmium metal weighed 0.2400 gram.

It will be noticed that the error in the results is fully within the limit. Cadmium was not detected in the filtrate.

The deposits in both experiments were very crystalline. Hot water was employed in washing the metal. The drying was done upon a warm iron plate. The current was invariably increased for about an hour before its final interruption. The acid liquid was syphoned off from the metallic deposit before the vessel in which the precipitation occurred was disconnected.

Some of the heavier metals were studied in the same manner as copper and cadmium. The results of this study are given below. They are new and have value for the student of electrolysis.

*Platinum.*

0.2590 gram. of ammonio-platinum chloride was dissolved in water. To this solution I added 30 c.c. disodium phosphate (sp. gr., 1.0358), 5 c.c. phosphoric acid, and diluted with water to 150 c.c. A current liberating 0.8 c.c. OH gas per minute acted upon the solution for a period of ten hours. The precipitated platinum metal was quite adherent. It was washed with water and alcohol. It weighed 0.1140 gram. The calculated amount of platinum corresponding to the quantity of double salt used in the trial is 0.1144 gram. The error is therefore 0.0004 gram.

Two additional trials gave 0.1255 gram. and 0.1263 gram. metal. The required quantity of platinum was 0.1260 gram.

The filtrates from these deposits were not discoloured upon the addition of hydrogen sulphide. The precipitated metal was deposited upon a copper-coated platinum surface.

A current best suited for the precipitation of 0.1-0.2 gram. metallic platinum should give about 0.4 c.c. oxyhydrogen gas per minute. If the current exceeds 0.7-0.8 c.c. OH

gas per minute, the platinum is apt to separate in a spongy condition, and when the current falls at low as 0.2 c.c. OH gas per minute, the copper coating dissolves.

Platinum is deposited very rapidly from its acid phosphate solution by the current.

The conditions outlined above allow of the electrolytic separation of platinum from the metals of the third and fourth groups.

#### *Palladium.*

This metal, under the influence of the current, separates very rapidly from a solution containing free phosphoric acid. The deposition is also complete.

1. A solution containing 0.1825 gram. palladium, 20 c.c. disodium phosphate (sp. gr., 1.0358), 5 c.c. phosphoric acid (sp. gr., 1.347), and 125 c.c. of water was electrolysed with a current giving 0.7 c.c. OH gas per minute. The deposited metal weighed 0.1817 gram. It was washed with hot water. The deposition was made upon a copper-coated platinum dish.

2. The conditions of experiment were analogous to those in 1. The precipitated platinum weighed 0.1830 gram.

In each instance the deposit of metal was compact and adherent. It resembled ordinary sheet palladium in appearance after it was dried.

The efforts made to separate palladium from cadmium, zinc and other metals were fruitless. The palladium was always fully precipitated, but it either carried down with it as much as 3 per cent. of the associated metal, or it separated in spongy, black masses. For the present the acid phosphate solution of palladium can only be recommended for electrolysis when other metals are not present with the palladium.

#### *Gold.*

1. The solution contained 0.1338 gram. gold, 20 c.c. disodium phosphate (sp. gr., 1.038), and 3 c.c. phosphoric acid (sp. gr., 1.347). Total dilution, 160 c.c. Current, 0.8 c.c. OH gas per minute. The metal was deposited upon copper. The deposit weighed 0.1335 gram. The filtrate was found free from gold.

The metallic deposit was quite adherent and compact. It was washed with hot water.

2. The conditions were similar to those just mentioned under 1. The gold deposit weighed 0.1339 gram.

Trials made for the purpose of separating gold from cadmium were not successful. The same behaviour was observed here as with palladium and cadmium. The gold separated completely from the solution, but it either carried down cadmium or it separated in a spongy mass. This last occurrence was always noticed when the quantity of phosphoric acid was increased.

I failed to separate palladium from zinc, notwithstanding the conditions were repeatedly modified. With gold and zinc the separation proceeded without the least difficulty.

#### *Gold from Zinc.*

A solution of 150 c.c. volume contained 0.1338 gram. gold, 0.1500 gram. zinc, 30 c.c. disodium phosphate (sp. gr., 1.0358), and 3 c.c. phosphoric acid. It was electrolysed with a current giving 0.6 c.c. OH gas per minute. The gold deposit was compact, and readily washed with hot water. It was dried over a warm iron plate. It weighed 0.1338 gram. Zinc was not precipitated.

*Gold from Cobalt.*

The quantity of metallic gold present was the same as in the preceding separation. The metallic cobalt was 0.2300 gram. The conditions, in all other respects, were the same as in the separation of gold from zinc. The precipitated gold weighed 0.1338 gram.

The current employed in the experiments recorded in this communication was derived from the "crowfoot" cells of the ordinary form. The flat platinum spiral in connection with the anode of the battery was  $1\frac{3}{4}$  inches from the cathode dish, in which the depositions of metal were made. All the precipitations occurred at the ordinary temperature.

The electrolysis of zinc, nickel, cobalt and iron phosphates, in acid solution, has thus far not yielded very encouraging results. Strong currents seem necessary. Even then the deposition of the metals is rather slow.

### REPORT OF RECENT RESEARCHES AND IMPROVEMENTS IN ANALYTICAL PROCESSES.

NEW METHOD FOR THE ANALYSIS OF PEPTONES. BY A. DENAEYER, BRUSSELS (*Bulletin de l'Association Belge des Chimistes*, 1st Dec., 1890). The author has modified the method previously described by him (*THE ANALYST*, June, 1890), further researches having shown that it was in several respects capable of improvement. During the peptic digestion of meat the gelatine of the connective tissue undergoes a more or less complete chemical change. When the action of acid pepsine at a temperature of 40°—45°C. is carried to its extreme limit, the whole of the gelatine is transformed into an allotropic, non-jellifiable variety which is soluble in alcohol. In ordinary peptones both kinds of gelatine are commonly present. They contain 15.3 per cent. nitrogen, whereas albumose and peptone only contain 17 per cent., and as they are not originally assimilable, it is evident that any analysis in which they are confounded with true peptone is of little value. In its present form the method is as follows:—

1. A carefully filtered solution of 2 grams. of dry peptone in 10 grams. of water is treated with 90 grams. alcohol of 90°. After standing for twenty-four hours the precipitate is washed with alcohol. It consists of albumen, albumose, peptone, and normal jellifiable gelatine.

The filtrate is reserved for process 6.

2. *For albumen.* The above precipitate is digested with hot water, and washed on a tared filter. The residue is dried and weighed as albumen, which was rendered insoluble by the alcohol.

3. *For normal gelatine.* The filtrate from albumen is treated with excess of neutral solution of mercuric chloride (instead of double iodide of mercury and potassium as formerly). This throws down albumose and peptone, but not gelatine. Ppt. rejected.

The solution containing  $\text{HgCl}_2$  is now treated in a tared beaker with excess of ammonium sulphate in crystals, boiled and cooled. Gelatine adheres to the beaker and may be washed with  $(\text{NH}_4)_2\text{SO}_4$ , dried and weighed. It is then dissolved in hot water diluted to 100 c.c., the ammonium sulphate estimated by standard barium chloride, and its weight deducted from the gelatine.

4. *For albumose.* A fresh portion is treated successively with alcohol and water, as in 1 and 2. The aqueous solution of albumose, peptone, and gelatine is treated as before, with excess of  $(\text{NH}_4)_2 \text{SO}_4$ . This throws down albumose and gelatine, *but not peptone*. The precipitate is collected partly on a tared filter, and partly in a tared beaker. After washing with  $(\text{NH}_4)_2 \text{SO}_4$ , the sulphate is estimated and deducted as before. Then the gelatine being known, albumose is found by difference.

5. *For peptone.* An aqueous solution of albumose, peptone, and gelatine is prepared as before. This is treated with excess of solution of phosphotungstate of soda, prepared as follows:—Tungstate of soda, 50 grams.; boiling distilled water, 1,000 grams.; phosphoric acid, 100 grams.; hydrochloric acid, 150 grams.; acid added after cooled, and solution filtered after twenty-four hours. This reagent throws down all three of the nitrogenous compounds. After settlement and partial decantation the precipitate is thrown on a tared Schleicher's filter, washed with dilute hydrochloric acid, dried and weighed. It is then incinerated, and the weight of the precipitate—*minus* the ash—gives the three ingredients, and, of course, the peptone by difference.

6. *For non-jellifiable gelatine and extractives.* The alcoholic solution (1) is divided into two portions. One of these is evaporated, the residue extracted with water, and the gelatine estimated as before by means of ammonium sulphate. The other may be evaporated to dryness and weighed, but as the residue is very hygroscopic, it is better to estimate the extractive matters by difference.

In addition to this method of analysis, M. Denaeyer's paper contains much that is important with regard to the albumens of meat preparations and the processes by which they can be separated; but for further details we must refer to the original paper, a translation of which has recently been published in pamphlet form by Messrs. Straker and Sons, Fenchurch Street, London.

C. W. H.

TANNATE OF QUININE. DR. J. E. DE VRY. (*Ned Tydschr v. Pharmacie*, etc. April, 1891.)—This compound is supposed to get a dirty colour when thoroughly dried, and the commercial product, therefore, generally contains some water, sometimes as much as 8 per cent. The author, however, found a thorough drying on the water-bath to yield an almost white product. To ascertain its purity the amount of quinine must be estimated as follows: Two grams. of the sample are shaken up in a separating funnel with 16 c.c. of cold water. When thoroughly mixed, 5 c.c. of soda ley are added and 30 c.c. of ether, and the whole well shaken. As ether is somewhat soluble in water, this will retain some ether, and consequently some quinine, which may, however, be completely removed by a second agitation with 30 c.c. of fresh ether. The quinine left on evaporation of the ether is then weighed, but must be further tested as to its purity. The author now makes it into sulphate, and then examines this by his *chromate* method, a full description of which will be found in *THE ANALYST*, 1889.

L. DE K.

ON SOURCES OF ERRORS IN THE ESTIMATION OF ZINC BY MEANS OF FERROCYANIDE. DR. F. MOLDENHAUER. (*Chem. Zeit.*, No. 14, 1891.)—The estimation of zinc by means of ferrocyanide, with copper sulphate paper as indicator, has gradually superseded the time-honoured titration with sodium sulphide. The process, however, like many others, is occasionally found wanting. The author has studied the influence of the presence of some other metals. Of the alkaline earths and lighter metals, there are only two whose ferrocyanides are quite insoluble in ammonia, viz., zinc and manganese. This magnesia compound is but little soluble. To see if it is possible to titrate zinc when mixed with lime, strontia, alumina, iron, and lead, several mixtures were made, and it seemed quite



possible to get a fair estimation of the zinc in presence of these metals. The presence of such ferric oxide only slightly influenced the result. But it is different in the case of magnesia and manganese. Of these bodies a not inconsiderable amount is precipitated by the ferrocyanide, and the amount of zinc may, in consequence, be found from 3 to 6 per cent. too high. After many experiments, the author has now finally adopted the following process:—

2·5 grams. of the ore are dissolved in hydrochloric acid, oxidised with nitric acid, and, without filtering, diluted up to 250 c.c. 50 c.c. of this solution are put into a flask and mixed with 10 c.c. of ammonia and 5 c.c. of a solution containing 5 grams. of officinal ammonium carbonate, 5 grams. of ammonium chloride, 10 c.c. of ammonia, and 90 c.c. of water. To make the precipitate settle, the liquid is heated. In the meanwhile 25 c.c. of the original solution are mixed with 10 c.c. of ammonia and titrated with ferrocyanide to get an idea how much it takes. Another 25 c.c. may then be titrated more accurately.

To the 50 c.c. of the fluid, which has now had time to cool, 2 c.c. of a 10 per cent solution of sodium phosphate are added. This will cause both the magnesia and manganese to separate out as phosphates. If no separation takes place, the titration with the ferrocyanide ought to give the same percentage of zinc as before, but if there should have been Mg. or Mn. the result, although lower than the first, should be taken as the true one.

The test analysis is very satisfactory.

L. DE K.

**ROESE'S PROCESS FOR THE ESTIMATION OF ALCOHOL.** R. BENEDIKT (*Chem. Zeit.*, No. 4, '91).—Dr. Roese has recommended a process for the estimation of alcohol, based on its complete oxidation to carbonic acid, by means of permanganate. In a tared flask, 5 c.c. of the 1 per cent. solution of alcohol are mixed with 50 c.c. of a 1 per cent. solution of permanganate and then with 20 c.c. of strong sulphuric acid, delivered from a pipette. After a minute, 100 c.c. of water are added, and then an excess of  $\frac{N}{10}$  solution of potassium tetra-oxalate; the liquid heated to boiling and checked back with permanganate.

Although the author worked exactly according to Roese's directions, he has obtained no satisfactory results. The strength of his solutions was practically the same as of those employed by Roese, 50 c.c. oxalic solution requiring 15·5 c.c. of permanganate.

If 50 c.c. of the permanganate are mixed with even only 10 c.c. of sulphuric acid instead of 20, the permanganate is rapidly decomposed and deposits manganic peroxide. In presence of spirit, one also obtains a turbid liquid which requires much more oxalate to clear up than Roese believes, showing that all the alcohol has not been oxidised. The comparison of the following figures shows the author's numbers to widely differ from Roese's:—

|                                  |    | Roese.   |    | Benedikt.                       |
|----------------------------------|----|----------|----|---------------------------------|
| 1 per cent. alcohol              | .. | 5·002    | .. | 5·0102                          |
| $C_2H_6O$                        | .. | ·05002   | .. | ·0501                           |
| Permanganate used                | .. | 50 c.c.  | .. | 50 c.c.                         |
| Checked back with                | .. | 5·6 c.c. | .. | 3·6 c.c.                        |
|                                  |    | <hr/>    |    | <hr/>                           |
|                                  |    | 55·60    |    | 53·60                           |
| Allowance for 50 c.c. of oxalate |    | 15·37    |    | 26·04 (for 84 c.c. of oxalate.) |
|                                  |    | <hr/>    |    | <hr/>                           |
| Reduced by alcohol               | .. | 40·23    | .. | 27·56                           |
| = Alcohol                        | .. | ·050     | .. | ·034                            |

L. DE K.

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## TO OUR READERS.

THE issue of this number marks an epoch in the existence of the ANALYST, because it is the last that will appear under the direction of the present Editor, who now, after nearly sixteen years of office, bids his readers farewell. Those who have followed the Journal from its commencement will be aware that it was originally started in the year 1877, by the Society of Public Analysts, and was at first conducted by the late Mr. Wigner and the present Editor, assisted by a Committee of Publication. After some time, the losses upon its production became too great for the funds of a Society then only limited in membership, and consequently the Editors took the paper off its hands and conducted it at their own risk. At Mr. Wigner's death the property passed entirely into the hands of the present Editor, who has conducted it ever since, and has succeeded in converting it from a commercial loss into a self-supporting publication. This being so, and the end for which he has always worked being attained, he decided to ask the Society to become once more the custodians of their Journal and to relieve him of the responsibility both of Editorship and Proprietorship. The Society having thus taken up their own burden he breathes a sigh of relief, but yet cannot help expressing his regret in parting both with his subscribers and with the *confreres* who have aided him in his self-appointed task of establishing a Journal devoted to the Improvement of Food Analysis.

The days of chemical politics are over, but the Editor can only look back with satisfaction on the time when the establishment of the Institute of Chemistry on its present basis was actively opposed in these columns. It was then argued by this Journal along that the basis of the Institute was bad, and that if it were to be a real benefit to analytical chemists, its foundation should have been on a nucleus of practising analysts (such as the Society of Public Analysts), and the professorial and trade elements it now contains should have been eliminated. As time goes on the views then expressed have come to be recognised by nearly all analysts, and an effort is being made to bring the Institute more within the lines of their needs, but with what effect remains to be seen, because so many of its present members are in no sense practising analytical chemists, but simply teachers, and even, in some cases, manufacturers or persons practically engaged in trade who have no real interests in common with the very men for whose supposed benefit it was projected.

It is an old Americanism to say that "every citizen thinks he can run a journal," and we hope that those who are now about to try their hands on this one will succeed in producing a much more ideal print than it has hitherto been. If they wish to do so, they will have to resist the blandishments on the one side of those who want to alter what they said imprudently, and on the other the threats of libel actions from those who object to the publication of what some one else said at the meetings about them. Of

both of these sensations the present Editor has had ample experience, even, on one occasion, to the extent of such threats from the then President of the Society himself. A committee has no body to assault and no soul to condemn, so that it will be able possibly to take a more independent ground than can ever be occupied by one man in such a position.

With these remarks, the Editor bids his readers farewell, and introduces the new Editorial Committee of the Society of Public Analysts.

### PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

AN ordinary meeting was held at Burlington House, on Wednesday, the 6th ult., the President, Mr. Hohner, in the chair.

The minutes of the previous meeting were read and confirmed.

Mr. Rymer-Paterson, B.Sc.Edin., was proposed for election as a member.

The President requested the Past-President, Mr. Adams, to take the chair whilst the first business on the paper was proceeded with.

Mr. Adams then took the chair, and a resolution was moved, seconded, and carried unanimously, removing the name of a member from the roll of the Society.

Mr. Hohner then resumed the chair, and the following paper was read:—"On the Examination of Spirituous Liquids for Secondary Constituents," by A. H. Allen and W. Chattaway.

The next meeting of the Society will be held on Wednesday, the 3rd inst.

### ON THE EXAMINATION OF SPIRITUOUS LIQUIDS FOR SECONDARY CONSTITUENTS.

BY ALFRED H. ALLEN AND WILLIAM CHATTAWAY.

*(Read at Meeting, May, 6th, 1891.)*

For many months past we have had in progress a series of experiments connected with the chemistry of whisky, having mainly for their object the examination of whisky and other spirituous liquids for secondary constituents.

The secondary constituents of spirits are by no means to be regarded in the light of impurities, as they have wrongly been called and considered by some. They are the associated bodies which give the alcohol its special and valued characters, and to their production, modification, or elimination by age we owe the changes which spirits undergo during the process of maturing.

The secondary or bye products of spirits are naturally most abundant in those spirituous liquids manufactured in apparatus where no, or but little, fractionation occurs. This is the case with the spirit distilled in Scotland in pot-stills, and made wholly from fermented malt, and in Ireland from a mixture of malted and unmalted barley, with, in some cases, a small addition of other grain. In the manufacture of whisky by the pot-still, the fermented wash is simply distilled over a naked fire, when "low wines" is obtained as a first product, the "pot ale" remaining in the retort being run to waste. On redistilling the "low wines" the first fraction which passes over is called "foreshots," the second "clean spirit," and the third "feints," while the residue in the retort is called "spent lees." The foreshots and feints become milky when mixed with an equal measure of water, and are mixed with the low wines of the next period to

be redistilled. It follows that whisky and spent lees (which is practically free from alcohol) are the only final products of the manufacture of spirit by the pot-still process. No fusel oil or other special product is obtained.

In the manufacture of spirit by the Coffey and other patent stills, in which fractionation is effected, the materials used for the production of the spirit are of a much more varied character. In the United Kingdom, a mixture is employed of malted and unmalted grain, maize, and rice, with, in some instances, sugar and molasses, only enough malt being used to effect the conversion of the starch to maltose. No potatoes, turnips, beets, or other roots are used in this country for the production of spirits, though such materials are largely employed on the Continent. The source of the spirit is evident to the expert only if imperfectly rectified, the best "silent spirit" affording no indication of its origin. But there is as much, or even greater, difference between the finest silent spirit, by which nearly chemically pure alcohol is to be understood, and spirit made from grain in the Coffey still, as there is between the latter and real pot-still whisky.

Pot-still spirit containing the largest proportions of those secondary constituents which give to properly-matured spirits their special value, it follows that the process of ageing and maturing is specially applicable to such products, which are:—Scotch and Irish whiskies made in pot-stills, wine-brandy, and real rum from sugar products. Factitious rum concocted from alcohol and flavouring agents would not come under this category; nor does patent-still whisky undergo anything like the same improvement by maturing as pot-still whisky. Brandy is a term now very much misused. It was formerly applied almost exclusively to cognac or French brandy, a product obtained by the distillation of wine or grape-skins. The German word *Branntwein* is now, unfortunately, commonly translated "brandy," although in the original language it has a far wider meaning than that we give to the term brandy.

The table on pages 110 and 111 shows the names and leading properties of the chief constituents of spirituous liquids.

Many of the bodies in the foregoing table exist in spirituous liquids in very minute amount, and their presence has never been detected in the spirit itself, but only in the fusel oil obtained by fractionating a large quantity of the alcoholic liquid.

According to L. Lindet (*Compt. rend.*, cxii., 102), the production of higher alcohols is very slow at first, but increases with the progress of the fermentation, and continues with still greater rapidity after fermentation proper has ceased. The proportions of "higher alcohols" (query, total oily matters) per litre were found in one case to be as follow: 14 hours, 3.64 c.c.; 20 hours, 4.45; 38 hours (fermentation complete), 6.44 c.c.; 62 hours, 9.2 c.c. The formation of the higher alcohols appears, therefore, to depend chiefly upon those abnormal conditions of yeast-life consequent upon the disappearance of the sugar. They may also be produced by some special organism which remains almost inactive in presence of the rapidly-developing and vigorous yeast, but becomes active when the work of the yeast is finished. Hence, the longer the time between fermentation and distillation, the larger the proportion of higher alcohols is likely to be.

It is a curious fact that the species of ferment affects the character of the higher alcohols produced. Thus the *saccharomyces cerevisiæ* of ordinary brewers' yeast produces

subsidiary products differing in certain important respects from those of *saccharomyces ellipsoides*, which is the ferment of grape-skins. In fact, it has been found that by adding the latter ferment to molasses and other saccharine liquids distinct from grape-juice, the product of the fermentation, after distillation, has all the characters of Cognac brandy. The most marked distinction between the subsidiary products of the two ferments is that whereas in the case of the grape-juice ferment *normal* butyl alcohol results, in other cases this is replaced by *iso*-butyl alcohol.

By the fractional distillation of Cognac brandy, twenty-five years old, Ordonneau obtained the following substances (*Compt. rend.*, cii., 217) :—

|  |    |    |    |    |    | Grammes per 100 litres. |
|--|----|----|----|----|----|-------------------------|
| Normal propyl alcohol                      | .. | .. | .. | .. | .. | 40.0                    |
| Normal butyl alcohol                       | .. | .. | .. | .. | .. | 218.6                   |
| Amyl alcohol                               | .. | .. | .. | .. | .. | 83.8                    |
| Hexyl alcohol                              | .. | .. | .. | .. | .. | 0.6                     |
| Heptyl alcohol                             | .. | .. | .. | .. | .. | 1.5                     |
| Ethyl acetate                              | .. | .. | .. | .. | .. | 35.0                    |
| Ethyl propionate, butyrate, and caproate.. | .. | .. | .. | .. | .. | 3.0                     |
| Enanthic ether (about)                     | .. | .. | .. | .. | .. | 4.0                     |
| Aldehyde                                   | .. | .. | .. | .. | .. | 3.0                     |
| Acetal                                     | .. | .. | .. | .. | .. | traces.                 |
| Amines                                     | .. | .. | .. | .. | .. | traces.                 |

Ordonneau's results have been substantially confirmed by Clandon and Morin (*Compt. rend.*, civ., 1187), who found the percentage composition of the same fusel oil to be as follows :—

|                      |       | Clandon and Morin. | Ordonneau. |
|----------------------|-------|--------------------|------------|
| Propyl alcohol       | .. .. | 11.9               | 11.7       |
| Normal butyl alcohol | .. .. | 49.3               | 63.8       |
| Isobutyl alcohol     | .. .. | 4.5                | 0.0        |
| Amyl alcohol         | .. .. | 34.4               | 24.5       |

The following proportions of various alcohols, etc., were obtained by Rabuteau (*Compt. rend.*, lxxxvii., 501) from 1 litre of potato fusel oil :—

|  |       |          |
|--|-------|----------|
| Iso-propyl alcohol..                       | .. .. | 150 c.c. |
| Normal propyl alcohol                      | .. .. | 30 "     |
| Iso-butyl alcohol ..                       | .. .. | 50 "     |
| Normal butyl alcohol                       | .. .. | 65 "     |
| Methyl-propyl-carbinol                     | .. .. | 60 "     |
| Iso-amyl alcohol ..                        | .. .. | 275 "    |
| Products boiling above 132°, and retaining |       |          |
| amyl alcohol ..                            | .. .. | 170 "    |
| Ethyl alcohol, aldehyde, and ethyl acetate | .. .. | 75 "     |
| Water ..                                   | .. .. | 125 "    |

Trimethyl-carbinol also appears to have been present.

The fusel oil produced in Chicago, from a spirit derived from maize with smaller quantities of other grains, has been examined by Long and Linebarger (*American Journ. Anal. Chem.*, January, 1890). The specific gravity of the water-saturated oil was 0.810 at 20° C. It was found impossible to dry it completely by anhydrous sulphate of copper, but a subsequent treatment for two hours at 40 to 50° C. with dry potassium carbonate removed the remainder of the water. Only a very inconsiderable portion of the oil boiled at a higher temperature than 133° C. It consisted in part of

alcohols and in part of bodies of an ethereal nature, the amounts of which were too small for their identification. About three-fourths of the sample consisted of a mixture of inactive and active amylic alcohols, with possibly some of the isomeric methyl-propyl carbinol. Iso-butyl alcohol appeared to be present in next largest amount, and after that iso-propyl and ethyl alcohols, with traces of normal propyl and normal butyl alcohols.

It seemed to us not improbable that spirituous liquids contained more than mere traces of propylic alcohol. This constituent, if present, would be very difficult to detect, and hence was likely to have been missed by previous observers, though, as a matter of fact, it is known to be produced by the alcoholic fermentation, and is stated to be isolated in Germany, as a commercial product, by fractionation of the feints from ordinary crude spirit. Any ordinary amount of fractionation, however, would be quite inadequate to isolate propylic alcohol or even to demonstrate its presence.

E. T. Chapman describes propylic alcohol as the most hygroscopic substance in his experience; so that the last traces of water present in an alcoholic liquid would adhere to it. Its boiling-point is only  $19^{\circ}$  above that of ordinary alcohol, and its solubility in water would cause it to be washed out from any fusel oil with great facility in which it existed. Iso-propyl alcohol boils at a still lower temperature ( $83-84^{\circ}$ ), and forms a hydrate,  $2C_3H_7O + H_2O$ , boiling constantly at  $80^{\circ}$ , and having the same percentage composition as ethyl alcohol. According to Linnemann, other hydrates also exist, boiling respectively at  $78^{\circ}$  to  $80^{\circ}$  and  $81^{\circ}$  to  $82^{\circ}$ .

In any attempt to separate the constituents of spirituous liquids by fractional distillation, it is necessary first of all to get rid of the water. Potassium carbonate removes the water very incompletely, even after protracted digestion, and the action of anhydrous copper sulphate is admittedly imperfect. Quick-lime and anhydrous baryta are more perfect dehydrating agents, and when the latter is used the completion of the process is said to be rendered evident by the solution of the baryta in the absolute alcohol, with yellow colour. We found baryta unavailable at the time we were making the experiments in question, owing to the impossibility of preparing it with the appliances at hand free from any trace of barium dioxide, which impurity rendered it unsuitable for our purpose. With quick-lime we obtained a spirit containing between 98 and 99 per cent. of absolute alcohol, as estimated from the specific gravity, and which boiled at an absolutely constant temperature from first to last. The spirit, after treatment with lime, appeared to be pure alcohol, and was wholly free from the characteristic flavour of the whisky with which we started. As this result was fatal to certain of the aims we had in view, the experiments in this direction were discontinued. A process appears to be still wanting which will effect a complete separation of water from alcohol without at the same time affecting any aldehydes or ethers which may be present.

Our idea that propyl alcohol might perhaps exist, to a notable extent, in spirituous liquids appeared to receive some confirmation from certain experiments of the President. Mr. Hehner, in a paper read before this Society (ANALYST xii., 25) described a process of estimating alcohol by treating the spirit with a known amount of standard chromic acid mixture, determining the excess of the latter by ferrous sulphate, and from the difference calculating the alcohol oxidised. The process possesses the advantage that the

homologues of alcohol require for their oxidation very different amounts of chromic acid from ethyl alcohol itself. Thus 100 parts methyl alcohol react with 922·4 parts of  $K_2Cr_2O_7$  (to form  $CO_2 + 2 H_2O$ ), while 100 of ethyl alcohol require but 427·8 parts (for the reaction  $C_2H_5O + O_2 = C_2H_4O_2 + H_2O$ ) and 100 of propyl alcohol only 328 parts (to form  $C H_3O_2$ ). Mr. H $\ddot{e}$ hner found several samples of whisky and brandy to consume an amount of bichromate considerably (5 to 7 per cent.) less than corresponded to the alcohol present, as ascertained from the specific gravity, a result which pointed to the presence of a notable proportion of propylic alcohol or other higher homologue. A limited number of experiments in this direction have not led us to the same conclusion. On the other hand, we find H $\ddot{e}$ hner's process, when conducted under favourable conditions, an exceedingly accurate method of estimating ethyl alcohol; and as our method of working differs in certain respects from his, and we consider the modifications of importance in obtaining accurate results, we give the mode of manipulation in detail:—

The alcoholic liquid is distilled to separate sugar, tannin, and extractive matter. The specific gravity of the distilled spirit is then determined very carefully with the bottle, and a weighed portion of it is diluted with a weighed quantity of water, so that 50 c.c. of the dilute liquid will contain approximately 0·2 gram. of absolute alcohol. The strength of the dilute spirit is confirmed by observing its specific gravity, and in our experiments the contained alcohol corresponding to this figure has coincided *absolutely* with the alcohol calculated from the known quantities of strong spirit and water employed. Exactly 2·400 grammes of solid potassium bichromate was introduced next into a stoppered bottle. The reagent had been carefully recrystallised and fused in porcelain at a gentle heat before use. 10 c.c. of dilute sulphuric acid (containing 3 grams. of strong sulphuric acid per 10 c.c.) was next added, and then exactly 50 c.c. of the dilute alcoholic liquid of known strength run in from a pipette. The bottle was then securely closed and kept at 100° C. for four hours. After cooling, an approximately  $\frac{N}{5}$  solution of ammonio-ferrous sulphate (78·4 grammes of  $FeSO_4 + (NH_4)_2 SO_4 + 6 H_2O$  per litre) was added in quantity just sufficient to reduce the potassium bichromate originally used. Of course, the exact deoxidising power of the iron solution must have been previously ascertained by reaction with the bichromate. In practice, we find that more accurate results are obtained by weighing the iron solution than by measuring it. More dilute sulphuric acid was then added, and the excess of reducing agent determined by titration with  $\frac{N}{5}$  potassium bichromate (9·837 grammes of  $K_2Cr_2O_7$  per litre). Each c.c. of  $\frac{N}{5}$  bichromate corresponds to 0·0023 gram. of ethyl alcohol.

Working in this manner on pure ethylic alcohol, and varying the proportions of bichromate and acid, we obtained the following results:—

| K $_2$ Cr $_2$ O $_7$<br>gramme. | H $_2$ SO $_4$<br>gramme. | Alcohol.          |         |             |
|----------------------------------|---------------------------|-------------------|---------|-------------|
|                                  |                           | Taken.<br>gramme. | Found.  |             |
|                                  |                           |                   | gramme. | = per cent. |
| 2·4                              | 3·0                       | ·2000             | ·2006   | 100·30      |
| 2 4                              | 5·5                       | ·2000             | ·2002   | 100·10      |
| 3·6                              | 4·5                       | ·2000             | ·2004   | 100·20      |
| 4·8                              | 6 0                       | ·2000             | ·2002   | 100·10      |

Two experiments were made on certain fractions obtained by the repeated distillation of whisky, which fractions were considered most likely to contain propylic alcohol. By the oxidation-process they showed 99·93 and 100·12 of ethylic alcohol, for 100·00 as determined by the specific gravity; so that, if propylic alcohol were present, the amount was too minute to be distinctly indicated by the process in question.

We have also tried the extent of accuracy of the bichromate titration process when applied to the estimation of amylic alcohol. A sample of fusel oil from beet-root spirit was dehydrated with lime and fractionated four or five times, with results showing that it consisted chiefly of iso-amyl alcohol, with lower but not higher homologues. After five very careful fractionations, no fraction of any size was obtained of a boiling-point higher than 128° C. When oxidised by chromic acid mixture, as above described, we obtained the following results:—

| Amylic Alcohol Taken. | Amylic Alcohol Found. |             |
|-----------------------|-----------------------|-------------|
| gramme.               | gramme.               | = per cent. |
| ·2590                 | ·2618                 | 101·08      |
| ·2600                 | ·2630                 | 101·15      |

These results show the probable presence of traces of butylic alcohol, as was also indicated by the boiling-point of the fraction.

The estimation of the amylic alcohol in commercial spirituous liquids has considerable interest and importance, and hence we have devoted much time and attention to the subject, with a view of finding or devising a thoroughly satisfactory process. In this connection, it is worthy of notice that, with the exception of a sample of Scotch whisky referred to by Dr. Dupré in a paper read before this Society in 1877 (*ANALYST*, i, 4), and a sample of potheen analysed by Sir Chas. Cameron, there was not, up to June of last year, a single published figure showing the proportion of fusel oil or higher alcohols in whisky. Various figures for brandy and potato-spirit, etc., have been published by Continental chemists, but whisky has been left severely alone.\*

One of the earliest chemical processes for the laboratory determination of amylic alcohol in spirits was that of Dr. A. Dupré, described before this Society in 1877 (*ANALYST* i. 4). It consisted in oxidising an amount of spirit containing from 1 to 2 grammes of alcohol with chromic acid mixture, neutralising nine-tenths of the volatile acids produced, and distilling, whereby the greater part of the acetic acid was got rid of as fixed sodium acetate, and the valeric acid concentrated in the distillate, which on

\* Early in last summer I was led to look carefully into the published statements respecting the proportion of fusel oil and amylic alcohol in whisky, and it was then that I discovered the paucity of information on the subject. A well-known firm of Irish distillers supplied a cask of whisky to a customer. When he had drunk the greater part of the whisky the customer refused to pay for it, alleging that it had made him ill; and when sued for the amount due brought a counter-action for injury to health, owing to his having been supplied with whisky containing "a large percentage" of fusel oil. This statement was scarcely borne out by his analyst, who had found 0·22 per cent. of amylic alcohol, while I, who had analysed the spirit on behalf of the distillers, had found but 0·07 per cent. In consequence of this discrepancy, the judge, at my suggestion, instructed us to make a joint analysis, the result of which was that we agreed that 0·07 per cent. was the correct figure.

As the amylic alcohol in spirits rarely exceeds 0·1 per cent., or 70 grains per proof gallon, it seems highly improbable that it can produce the local effects sometimes attributed to it. Its effect on the general system has probably been greatly exaggerated. A pupil of mine informs me that some years ago he took a teaspoonful of fusel oil, mixed with water, without any ill-effect. Recently, for three weeks I took every evening, with a few exceptions, a wine-glass full of whisky to which crude fusel oil had been added to the extent  $\frac{1}{2}$ , 1, and ultimately 2 per cent. The spirit was extremely nauseous, but produced no headache or other ill-effects.—A. H. ALLEN.



treatment with barium carbonate yielded the barium salts of the volatile acids contained in the fraction. The weight of these salts and the percentage of barium contained in them was then ascertained. As barium acetate contains 53.73 per cent. of Ba, while the valerate contains 40.41 per cent., it follows that the proportions of acetic and valeric acid in a mixture of the two can be determined by this means. Like all similar indirect methods the results are only reliable when neither constituent is in very large excess. Where the proportion of one ingredient is small, the method becomes untrustworthy. Thus Dupré obtained from the  $\frac{1}{10}$  fraction of the volatile acids resulting from the oxidation of a sample of Scotch whisky a mixed barium salt containing 53.49 per cent. of Ba. It is evident that this result indicates a very small proportion of valeric acid in the mixture, and hence a grave chance of error. But it is worthy of notice that the amylic alcohol calculated from the above result comes to 0.108 per cent. in the whisky, or 66.5 grains per proof gallon, a result which more modern methods confirms as a perfectly probable figure.

Dupré's process might, of course, be improved by a further concentration of the valeric acid by fractional neutralisation followed by distillation, but the process is even then objectionable on account of the small quantity of alcohol worked on, and which cannot be conveniently increased. If a sample of spirit of proof strength contain 0.1 per cent. of amylic alcohol, it is evident that by working on 3 grammes of the sample the valeric acid obtained will correspond only to 0.003 gramme of amylic alcohol, an amount altogether too small to give safe quantitative results.

A great improvement on Dupré's process has been made by L. Marquardt (*Berichte* xv. 1661), who operates on 150 grammes of the sample. This he dilutes with water till it has a specific gravity of .980 (corresponding to about  $28\frac{1}{2}$  per cent. of proof spirit, or 13 per cent. of alcohol by weight), and then repeatedly agitates with chloroform. This dissolves the fusel oil, while the traces of ethyl alcohol also taken up are removed by repeated agitation with water. The chloroform is then treated in a strong bottle or flask with 2 grammes of sulphuric acid and 5 grammes of potassium bichromate in 30 c.c. of water. The bottle is then securely closed and heated under pressure at 85°C., with frequent agitation, for six hours. It is then distilled to a small bulk, water added, and the distillation repeated. The mixed chloroform and aqueous distillate are boiled with barium carbonate under a reflux condenser, the chloroform distilled off, and the aqueous liquid concentrated and filtered from the excess of barium carbonate. The filtrate is evaporated to dryness and the residue weighed, after which it is redissolved, and the barium and chlorine determined in separate portions of the solution. From these data the weight of the valeric radical and the corresponding amylic alcohol can be deduced.

With care and good fortune we have found Marquardt's process capable of yielding very fair results, but the practical difficulties in properly carrying out the method are very considerable. In the first place it is extremely difficult to obtain chloroform of such purity that it will not yield a sensible quantity of volatile organic acid on treatment with chromic acid mixture. Although the chloroform used has been several times purified by heating with chromic acid mixture, it is still liable to give troublesome traces of volatile acids on retreatment. And even if such a purification be effected as to get rid of all but negligible traces of such impurities, a sensible amount of hydrochloric acid

is formed on oxidation, and this contaminates the barium salts, necessitates a determination of the chlorine, and a correction for the amount found. The necessity of treating the chloroformic solution with chromic acid mixture under pressure is also a serious objection to the process. The pressure at 85° is very considerable, and bursting of the bottle containing the mixture has happened not unfrequently. At any notably lower temperature the oxidation appears to be incomplete. The whole process is tedious, owing to the frequent agitations requisite, for the densities of the chloroform and chromic acid mixture are so different that the liquids separate almost instantly after agitation, and hence the reaction occurs but slowly. We have attempted to overcome the last difficulty by increasing the density of the chromic acid mixture till it is equal to that of chloroform, so as to obtain an emulsion on shaking, but even this device was only partially successful.

Owing to the difficulties attendant on the use of chloroform we have now definitely abandoned its use in favour of carbon tetrachloride. This liquid boils at 76·7°C., and hence the oxidation can be conducted under a reflux condenser at the ordinary atmospheric pressure; and as the vapour of the heavy chloride of carbon with its contained amylic alcohol is continually passing up through the layer of chromic acid mixture, proper contact is obtained and complete oxidation ensured without much personal attention being requisite. The carbon tetrachloride of commerce is obtained by a single treatment with chromic acid mixture in such a condition of purity that it yields no volatile organic acid on further oxidation and a mere trace of hydrochloric acid. It is a more expensive reagent than chloroform, but owing to its higher boiling point there is much less wasted in its use, and it is recovered practically without loss.

One curious difficulty has arisen in connection with the use of carbon tetrachloride, and that is the tendency of amylic alcohol to be partially removed from its solution therein by agitation with water, and hence to be only imperfectly extracted from the diluted spirit. This behaviour, which at one time appeared very formidable, we have completely overcome by the use of brine instead of water for diluting the spirit, and of brine or sodium sulphate solution for washing the carbon tetrachloride after the extraction. We have proved the competency of this mode of working in various ways.

The following are the details of the process for the determination of amylic alcohol in spirits as now worked by us. As a preliminary step, any fixed matters must be removed, and any ethers and furfural present destroyed in the following manner. The omission of this step is liable to cause the results obtained to be materially in excess of the truth, and invalidates the figures obtained by Dr. Bell and ourselves before the necessity of the precaution was pointed out by one of us (A. H. Allen).

100 c.c. measure of the spirit is taken, 20 c.c.  $\frac{N}{10}$  caustic soda added, and the whole heated under a reflux condenser for an hour. The contents of flask are then distilled in the following manner:—A volume of 90 c.c. is allowed to pass over, the flame is then removed, and 30 c.c. of water is introduced into distilling flask. The distillation is continued until 20 c.c. more has been collected. The distilling flask is allowed to cool, and 10 grams. sodium sulphate washed into the distilling flask with 20 c.c. more water. The distillation is again continued until 20 c.c. has passed over, thus bringing the total volume of the distillates to 130 c.c. By this time, all the amylic alcohol will have been volatilised:

## CHIEF CONSTITUENTS OF SPIRITS AND FUSEL OIL.

| Empirical formula.   | Name.                                       | Constitutional formula.                 | Boiling point. °C. |
|----------------------|---|---|--------------------|
| $C_2H_6O$ ..         | Ethyl alcohol .. ..                         | $CH_3CH_2OH$ .. ..                      | 78.4               |
| $C_3H_8O$ {          | Normal propyl alcohol .. ..                 | $CH_3CH_2CH_2OH$ .. ..                  | 98                 |
|                      | Iso-propyl alcohol .. ..                    | $(CH_3)_2:CH.OH$ .. ..                  | 83—84              |
| $C_4H_{10}O$ {       | $\alpha$ -Normal butyl alcohol .. ..        | $CH_3CH_2CH_2CH_2OH$ .. ..              | 117                |
|                      | $\beta$ -Iso-primary butyl alcohol .. ..    | $(CH_3)_2:CH.CH_2.OH$ .. ..             | 108—109            |
|                      | Tertiary butyl alcohol .. ..                | $(CH_3)_3:C.OH$ .. ..                   | —                  |
|                      | $\alpha$ -Normal primary amyl alcohol .. .. | $CH_3CH_2CH_2CH_2CH_2.OH$ .. ..         | 137—138            |
|                      | $\beta$ -Iso-primary amyl alcohol .. ..     | $(CH_3)_2:CH.CH_2CH_2.OH$ .. ..         | 131.4              |
| $C_5H_{12}O$ {       | $\gamma$ -Iso-primary amyl alcohol .. ..    | $(CH_3)(C_2H_5):CH.CH_2.OH$ .. ..       | 128                |
|                      | Methyl-propyl carbinol .. ..                | $(CH_3)(C_3H_7):CH.OH$ .. ..            | 119—120            |
| $C_6H_{14}O$ ..      | Iso-primary hexyl alcohol .. ..             | $(CH_3)_2:CH.CH_2CH_2CH_2.OH$ .. ..     | 152—153            |
| $C_7H_{16}O$ ..      | Iso-primary heptyl alcohol .. ..            | $(CH_3)_2:CH.CH_2CH_2CH_2CH_2.OH$ .. .. | 163—165            |
| $C_2H_4O_2$ ..       | Acetic acid .. ..                           | $CH_3CO.OH$ .. ..                       | 118                |
| $C_4H_8O_2$ ..       | Ethyl acetate .. ..                         | $C_2H_5.C_2H_3O_2$ .. ..                | 74.3               |
| $C_7H_{14}O_2$ ..    | Ethyl valerate .. ..                        | $C_2H_5.C_4H_7O_2$ .. ..                | 134.5              |
| $C_7H_{14}O_2$ ..    | Amyl acetate .. ..                          | $C_5H_{11}.C_2H_3O_2$ .. ..             | 137                |
| $C_{10}H_{20}O_2$ .. | Amyl valerate .. ..                         | $C_5H_{11}.C_4H_7O_2$ .. ..             | 188                |
| $C_2H_4O$ ..         | Aldehyde .. ..                              | $CH_3.CO.H$ .. ..                       | 21—22              |
| $C_3H_6O$ ..         | Acetone (occurrence doubtful) .. ..         | $CH_3.CO.CH_3$ .. ..                    | 56.5               |
| $C_6H_{14}O_2$ ..    | Acetal (diethyl-aldehyde) .. ..             | $CH_3CH:(O.C_2H_5)_2$ .. ..             | 104—106            |
| $C_6H_8O_4$ ..       | Furfural (furfuraldehyde) .. ..             | $C_4H_3O.CO.H$ .. ..                    | 161                |
| $C_5H_5N$ ..         | Pyridine .. ..                              | $C_5H_5N$ .. ..                         | 116.7              |

The mixed distillates are now diluted with saturated brine until the density of the liquid is about 1.10, when it is shaken four times successively with carbon tetrachloride, using 40 c.c. the first time, next 30 c.c., then 20 c.c., and lastly 10 c.c. The tetrachloride of carbon now contains the amylic alcohol and probably some ethylic alcohol, and with a view of removing the latter, it is shaken twice with 50 c.c. brine; or preferably, once with brine and once with a saturated solution of sodium sulphate, so as to avoid any traces of chlorides being present after separation. The carbon tetrachloride is finally run off from the separator and filtered.

The oxidation may be conducted in a closed bottle, or under a reflux condenser. The oxidising mixture consists of 5 grammes of potassium bichromate, 2 grammes concentrated sulphuric acid and 10 grammes of water. In using a closed bottle the oxidation is conducted in the water-oven, and it is necessary that the bottle be frequently agitated. Under these conditions the oxidation will be complete in four hours. When a flask is used, under a reflux condenser, the carbon tetrachloride should be kept in active ebullition for eight hours, this being best effected over a water-bath.

After oxidising, the product is diluted with 30 c.c. water and distilled over a naked

CHIEF CONSTITUENTS OF SPIRITS AND FUSEL OIL (*continued*).

| Action of $H_2SO_4$ on dilute alcoholic solution. | Products of treatment with caustic alkali. | Products of oxidation with dilute chromic acid mixture. |
|---|--|---|
| Not affected .. ..                                | } Not affected .. ..                       | Acetic acid.  |
| Not affected .. ..                                |  | Propionic acid.   |
| Not affected .. ..                                |  | Acetone; then acetic and carbonic acids.                |
| Not affected .. ..                                |  | Normal butyric acid.                                    |
| Strong coloration .. ..                           |  | Iso-butyric acid; then acetic and carbonic acids.       |
| —   |  | Acetic and carbonic acids.                              |
| —   |  | Normal valeric or pantoic acid.                         |
| Coloration .. ..                                  |  | Iso-valeric or pantoic acid (inactive).                 |
| —   |  | Dextro-rotatory valeric acid.                           |
| —   |  | Methyl-propyl-ketone; then acetic and propionic acids.  |
| Strong coloration .. ..                           |  | Iso-caproic acid.                                       |
| Strong coloration .. ..                           |  | Iso- <i>cananthylic</i> acid.                           |
| Not affected .. ..                                | Acetate .. ..                              | Unchanged (acetic acid).                                |
| Not affected .. ..                                | Acetate and ethyl alcohol .. ..            | Acetic acid.  |
| Not affected .. ..                                | Valerate and ethyl alcohol .. ..           | Acetic and valeric acids.                               |
| Coloration .. ..                                  | Acetate and amyl alcohol .. ..             | Valeric and acetic acids.                               |
| Coloration .. ..                                  | Valerate and amyl alcohol .. ..            | Valeric acid.   |
| Coloration .. ..                                  | Resin, acetate, and alcohol .. ..          | Acetic acid.  |
| Not affected .. ..                                | Not readily affected .. ..                 | Acetic and carbonic acids.                              |
| Forms alcohol and aldehyde                        | Not affected .. ..                         | Acetic acid.  |
| Strongly blackened ..                             | Pyromucate and furfuryl alcohol            | Pyromucic acid, $C_4H_5O.CO.OH$                         |
| Forms pyridine sulphate ..                        | Not affected .. ..                         | Not affected.   |

flame until only 20 c.c. remains in the distilling flask. 80 c.c. of water are now added, and the distillation continued until only 5 c.c. remains in the flask.

The distillate will now contain the whole of the valeric acid, a portion being in the aqueous distillate, and a portion in solution in the carbon tetrachloride. The *entire* distillate is now titrated with decinormal baryta-water, using methyl orange as an indicator, and shaking thoroughly after each addition. Not more than 2 c.c. of  $\frac{N}{10}$  alkali, and generally much less, ought to suffice to produce neutrality. Phenolphthalein is then added, and the titration continued with frequent shaking until the neutral point is again reached. Each c.c. of  $\frac{N}{10}$  alkali used in the second stage of the titration corresponds to 0.102 gramme of valeric acid or 0.088 gramme of amylic alcohol. The alkali consumed in the titration with methyl orange represents the *mineral acid* formed and is not, of course, taken into account.

The foregoing method of dealing with the products of the oxidation is a great improvement on that prescribed by Marquardt. It substitutes a rapid, easy, and delicate titration for a treatment with barium carbonate (and chance of imperfect neutralisation), followed by filtration, evaporation, drying, weighing, and supplementary determina-

tions of barium and chlorine. Nevertheless, the observation of the weight of the barium salts is often very valuable, as it enables the combining weight of the organic acid to be calculated, and its identity with valeric acid inferred. For this purpose, the neutralised aqueous liquid is separated from the carbon tetrachloride (which after a precautionary treatment with chromic acid mixture and distillation from barium carbonate can be used again) evaporated to dryness and the residual barium salt dried at  $100^{\circ}$  (or, preferably, at  $130^{\circ}$ ) and weighed. In the event of any notable quantity of mineral acid having been indicated, this weight must be corrected by the weight of barium chloride deduced from the result of the titration with methyl orange. In the absence of hydrochloric acid, or in its presence after making this correction, the mean combining weight of the organic acids can be found as follows:—

$$\frac{\text{Corrected weight of barium salt in milligrammes.}}{\text{Volume of normal baryta in c.c.}} - 67.5 = \text{comb. weight of organic acid.}$$

In experiments where we have added pure amylic alcohol to spirit with a view of testing the process, the organic acid obtained has had the characteristic odour of valeric acid and a combining weight closely approximating to 102.

In conducting the determination of amylic alcohol by the foregoing process, the following points must be observed:—

1. The carbon tetrachloride must be previously purified by treatment with chromic acid mixture and distillation over barium carbonate, and must be free from chloroform.

2. All corks used in distilling the spirit must be kept distinct from those employed in distilling the product of oxidation. In all cases, the corks must be carefully covered with tinfoil, or they will absorb amylic alcohol and valeric acid in quantity sufficient to vitiate the results.

3. A few small fragments of pumice-stone should be added, in each case, to the contents of the distilling flasks. The pumice employed with the oxidised liquid should be treated with chromic acid mixture before use.

4. The brine should be made from clean table-salt, rendered distinctly acid with sulphuric acid, and filtered before use.

Of course, the so-called estimation of amylic alcohol in spirits is in reality the estimation, in terms of amyl alcohol, of such higher alcohols and other bodies as may be extracted by chloroform or carbon tetrachloride, and converted into volatile organic acids on oxidation. But it is noticeable that the higher alcohols other than amylic alcohol will give products which do not materially affect the results. Thus isobutyl alcohol on oxidation yields isobutyric acid, which body undergoes further change into acetic and carbonic acids. But the acetic acid formed will neutralise just the same amount of alkali as the isobutyric acid would have done.

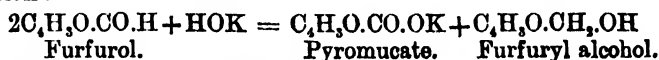
Dr. James Bell has modified Marquardt's process by using potassium permanganate in place of bichromate, and continuing the oxidation for a very long period. The change appears a very objectionable one. Permanganate of potassium is very liable to contain traces of perchlorate, which, being isomorphous, cannot be removed by any process of recrystallisation. On distillation with acid such impure permanganate yields distinct traces of perchloric acid (or other oxide of chlorine) which when boiled with barium carbonate yields a soluble salt, the acid in which has nearly the same combining weight as valeric acid ( $\text{HClO}_4 = 100.5$ ;  $\text{HC}_4\text{H}_7\text{O}_2 = 102$ ). Even pure permanganate appears to

act on chloroform far more readily than bichromate does, and on subsequently distilling the liquid a distillate is obtained having a yellow colour and strong chlorous odour.

Besides the various modifications of the oxidation process of estimating higher alcohols in spirits, certain physical methods have been suggested. We have tried the capillary method of Trauber, as modified by Elsworth (*Jour. Chem. Soc.*, liii. 102), but have not found it suitable for our purpose. The Rose-Herzfeld method, depending on the increase in the volume of chloroform when shaken with the spirit reduced to a constant strength, appeared more promising. But the absolute necessity of adjusting the strength of spirit accurately within the limits of 29.96 and 30.04 per cent. of absolute alcohol is a serious bar to the use of the process, which in the end gives rather an estimation of the total oily bodies present than of the higher alcohols, and fails even with these when the proportion is as low as commonly occurs in practice. We have met with more encouraging results by using carbon tetrachloride instead of chloroform, while the employment of brine for dilution renders the strength of the spirit immaterial within wide limits. But the process thus modified has not yet been perfected, and hence we postpone its description.

As already stated, the presence of ethers or furfural will invalidate the determination of amylic alcohol by oxidation, as these bodies are extracted both by chloroform and carbon tetrachloride, and on oxidation will yield organic acids. Thus ethyl acetate will yield two equivalents of acetic acid, and will falsify the amylic alcohol result to an extent equal to double its own weight.

The ethers of spirits can be determined (in terms of a typical compound such as ethyl acetate) by a process apparently originating with Berthelot, and applied by Dupré to the ethers of wine. It is substantially the same as was subsequently used by Koettstorfer for the examination of butter and other fats, and is based on the amount of alkali required for the saponification of the ether. But in the examination of spirits we are met with the difficulty that bodies of the type of aldehyde and furfural are present, and these also react with alkali. Aldehyde reacts with alkali with formation of aldehyde-resin and production of a formate and acetate, but the reaction does not appear to have been examined in its quantitative relationships, or to correspond to any simple formula. Furfural, however, has been found by Dr. A. Colefax, who has been working with us on the subject, to react with alkali almost strictly according to the following equation:—



It is probable that a determination of furfural might be based on this reaction. Fortunately, the error introduced into the determination of the ethers by the presence of aldehyde and furfural can be obviated by means recently described by E. Mohler, who has found that on digestion with a solution of aniline in syrupy phosphoric acid the aldehyde and furfural are converted into non-volatile compounds, while the ethers can be distilled off unchanged. We have fully confirmed Mohler's observation, provided that the treatment with the aniline reagent be conducted at the boiling point of the spirit, under a reflux condenser, for at least two hours. The following is the mode of operation:—

200 c.c. is distilled to about 20 c.c., when 50 c.c. measure of water is added, and the distillation continued till all but about 10 c.c. has passed over. The distillates are mixed and divided into two equal parts (A and B). One portion (A) is titrated with decinormal caustic alkali and phenolphthalein and the free acid thus found calculated to acetic acid. The neutral liquid is treated with 20 c.c. of  $\frac{N}{10}$  caustic alkali, and boiled under a reflux condenser for one hour, when the excess of alkali is ascertained by titra-

tion with decinormal acid. The other (B) portion of the distilled spirit is treated with 1 c.c. of aniline and 1 c.c. of phosphoric acid of 1.442 sp. gr., and boiled under a reflux condenser for at least two hours. It is then distilled to a low bulk, and the distillate neutralised and treated with 20 c.c. of  $\frac{N}{10}$  soda, exactly as was done with the other portion. The difference between the alkali added and that found by titration represents that consumed by the saponification of the ethers in 100 c.c. of the spirit; each c.c. of the decinormal alkali representing .0088 gramme of ethyl acetate.

The difference between the amounts of alkali required for the saponification of portions A and B represents the alkali which has reacted with furfural, aldehyde, etc., and, where only the first substance is present, 1 c.c. of  $\frac{N}{10}$  alkali represents 0.0192 gramme of furfural. The presence of furfural in spirits can be detected, and the proportion roughly guessed at, by the reaction of the sample with a solution of aniline in glacial acetic acid. Ten drops of aniline should be dissolved in 2 c.c. of glacial acetic acid, and the mixture added to 10 c.c. of the spirit to be tested. A red coloration is produced, which increases in intensity on standing. The reaction is peculiar to furfural and extremely delicate, one part per million giving a distinct coloration.

Aldehyde is best detected in spirits by Gayon's reagent consisting of 30 c.c. of a solution of magenta (rosaniline hydrochloride) in 1,000 parts of water; 20 c.c. of bisulphite of sodium solution (of 1.31 sp. gr.); 3 c.c. of sulphuric acid; and 200 c.c. of water. 4 c.c. of this mixture should be added to 10 c.c. of the spirit to be tested, when a crimson coloration is produced, increasing in intensity on standing:

According to Mohler, no satisfactory colorimetric determination can be based on this reaction, but the following proportions of aldehydes can be detected:—Acetic and cenanthic aldehydes, 0.01 gramme per litre; valeric aldehyde, 0.02; propionic and isobutyric, 0.05; normal butyric aldehyde, furfural, and acetone, 0.5 gramme per litre. Alcohols and ethers give no coloration with the rosaniline reagent, but it is difficult to meet with commercial alcohol so pure as to give a wholly negative reaction. It has been stated by Bornträger that the reagent is untrustworthy, as it merely indicates the presence of an oxidising agent; but this is evidently not the case, as the proportion of sulphite present is many times the amount requisite to prevent any oxidising action of the aldehyde.

At present there exists no satisfactory means of determining aldehyde in the minute quantities in which it exists in spirits. Its behaviour with alkalies to produce aldehyde resin and the accompanying odour is the most characteristic reaction.

Acetal is a body having the constitution of a diethyl-aldehydate. It has an agreeable odour, and is produced by the prolonged contact of aldehyde with alcohol, and hence has been recognised as a constituent of old wine and matured spirits. We have not been able to recognise its presence with certainty in the moderate quantities of spirits we have worked on. Acetal is unaffected by alkalies if air be excluded, but on treatment with dilute acid is at once split up into alcohol and aldehyde. Its most characteristic reaction is the formation of a colourless liquid with caustic soda and iodine solution, which yields a dense precipitate of iodoform when acidified. This reaction does not occur in very dilute solutions of acetal. Acetal is extracted by chloroform and carbon tetrachloride from its solution in dilute alcohol, and hence will affect the determination of the amylic alcohol if not previously got rid of, which may be done by first heating the spirit with an acid, and subsequently distilling with alkali.

Various methods of stating the results of analysis of spirituous liquids have been adopted. The statement in "parts per 100 of absolute alcohol" has certain merits; but in practice is less convenient than "parts per 100 of proof spirit." "Grammes per 100 c.c." and "grammes per litre" have the advantage of ready calculation, but statements

so made are apt to be misleading if the strength of the spirit is not also borne in mind. The statement in "grains per proof-gallon" has the advantage of defining the strength of the spirit, and avoids the long decimals necessary in other forms of statement.

Much still remains to be done before the methods of analysing spirituous liquids can be regarded as perfect, and still more before the results obtained can be properly interpreted. At present we can only claim to have fairly accurate processes for estimating the water, alcohol, higher alcohols, ethers, and free acid, with very delicate coloration tests for furfurol and aldehyde. But there are other bodies in spirit, the nature of which is only guessed at, and the presence of which is only indicated by the smell and flavour they impart to the liquid. The minute proportion in which these constituents exist, their unknown nature, the very large amount of spirit necessary for their isolation, and even for their concentration, will render their investigation extremely difficult.

#### DISCUSSION.

DR. DUPRE said, first, that he was perfectly willing to let his old process for determining amylic alcohol die in favour of a better one, but would like to know how it compared with the new. And, secondly, he must protest against the method of determining ethers based on their saponification being called Koettstorfer's method. It was brought out many years ago by Berthelot, and he (the speaker) was the first in this country to use it extensively; in fact, Koettstorfer's process of butter analysis was only a slight variation of a method which he (Dr. Dupré) brought before the Society at one of its earliest meetings.

The PRESIDENT pointed out that the usefulness of the Society had again been demonstrated by the authors, who, in their very excellent paper, had drawn upon the Society's work in several directions. He suggested that they might combine the process which they had adopted, viz., the determination of the volatile acids formed by oxidation by means of bichromate, with the modification of the bichromate process introduced by himself (Mr. Hehner), and estimate at the same time the amount of bichromate consumed. The measuring of the bichromate solution required great care, as had been pointed out by the authors; but if the temperature of the bichromate solution was taken into consideration, and care was taken to let the solution run out of the burette very slowly, perfectly accurate results could be obtained, although he himself had also, from time to time, employed weighed quantities of bichromate instead of a standard solution. He was glad that Mr. Allen was gradually helping to place the question of fusel oil in spirits on a scientific basis. Hitherto, all evil effects of some spirits had been attributed to fusel oil, although nothing definite was known about the real nature of the injurious constituents. It was a great step in advance, to come to a recognition of our ignorance in the matter, and to get rid of glib talk about fusel oil. In conclusion, he asked the members to accord their best thanks to the authors for their admirable paper, which was evidently based upon careful research and analysis.

MR. ALLEN, in reply, said they had undoubtedly been led to make the experiments on the estimation of alcohol by titration with bichromate, in consequence of Mr. Hehner's results. He thought Mr. Hehner's suggestion to combine the determination of the amount of oxygen taken up by the alcohol with a determination of the acid formed decidedly valuable in certain cases. Dr. Dupré's figures for amylic alcohol, published in 1887, were perfectly consistent with results more recently obtained by improved methods. With regard to the saponification method of determining ethers, one, of course, associated the process with the beautiful work done by Thudichum and Dupré in the analysis of wines.

*(Conclusion of the Society's Proceedings.)*



## THE DETECTION OF ANTISEPTICS IN BEERS.\*

BY DR. H. ELION.

ONE of the less agreeable duties which a brewer's chemist has now and then to perform is the analysis of samples of beer from other breweries, to see whether they use unfair means to make their inferior product saleable. If anything goes wrong with their beer, they are almost sure to use antiseptics.

A few years ago I published a process for the detection and approximate estimation of minute traces of salicylic acid, but as the use of this substance has been prohibited in several countries, it is now but very seldom used, other bodies being, however, substituted for it.

As I was lately again called upon to undertake the investigation of a similar product, I was thinking whether it would not be possible to find out a method to ascertain the presence of any antiseptic in a sample of beer, without pretending to say what preservative it really was. In the present state of our science it must not, of course, be expected to detect the most minute quantity; but as the object of using antiseptics is really to be able to sell a beer which would otherwise be condemned, the amount used will generally be fairly large. The antiseptics plainly serve to make the beer keep better; but in my opinion such simple means are in reality very unfair, as I wish to make plain, as follows:—A good beer must be right as regards odour, taste, colour, clearness, &c.; if a sample is supposed to keep well, this naturally means that it will retain these properties for a long time, even when kept under less favourable conditions. Pasteur has proved that, after a while, there form various micro-organisms, so-called *disease-ferments*, which make the beer unfit for consumption. While these are considered to be mostly bacteria, it must be remembered that beer may contain a peculiar yeast, which, under suitable conditions, may so multiply as to make the beer very turbid, and affects the taste of the article. It now mostly depends what treatment the beer undergoes after leaving the brewery. In England, for instance, it is quite customary to keep the beer in the barrel until used up. In this case a slight increase of the yeast, which goes to the bottom, is not only harmless, but even desirable to keep the beer well impregnated with carbonic acid. If beer is kept in bottles, the formation of yeast ought to be only very slight, otherwise it will be almost impossible to pour out a glass of clear beer. In properly conducted breweries, it is nowadays not so particularly difficult to prevent the growth of bacteria; but if great care is not taken the brewer will be obliged to stop their multiplication by the use of some antiseptic. The process which I have now worked out to detect such adulteration is as follows: On the fifth of November last year, I received some bottles of beer, which were said to keep particularly well, and this proved indeed to be the case in a high degree. Not only was the beer still quite clear on 21 December, but even last March, after standing for four months in the laboratory, it did not show any alteration. The deposit was so small as not to sensibly render the beer turbid on shaking. On the 21st of December I started the investigation. Under the microscope, the deposit showed an organism like *sarcina*, also a few bacilli, but scarcely any yeast cells. A portion of this beer was now introduced, with the usual precautions, in previously sterilised Pasteur's flasks, which were only half filled.

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\**Zeitschr. f. Angew. Chemie*, April, 1891 (slightly abridged).

In some of these flasks a trace of the *saccharomyces cerevisiae* was introduced, and the whole kept at a temperature of 25° C. In none of them any yeast was formed, pointing to three possible causes:—

1. The absence of fermentable sugar.
2. An insufficient amount of nourishment for the yeast.
3. The admixture of antiseptics.

The possibility of the increase in yeast being stopped by a large amount of alcohol was put out of the question by the analysis of the beer:

|                                     |                |
|-------------------------------------|----------------|
| Sp. gr. d $\frac{15}{18}$           | = 1.01454.     |
| Apparent extract (see my tables)... | 3.57 per cent. |
| Real extract...                     | ... 4.54 „     |

Which of the three causes was the true one was decided by adding to the contents of some of the flasks a previously sterilised solution of maltose, and also some yeast-food. But even after adding more of the *saccharomyces*, no formation of yeast cells were noticed, which plainly proved that the great durability of this beer was caused by the use of an antiseptic. The beer was now shaken out several times with an equal volume of ether, sterilised in Pasteur's flasks, and again treated with the *saccharomyces cerevisiae*. By the ether treatment the antiseptic (which was not salicylic acid) was removed, and a very active formation of yeast now set in. An estimation of the fermentable sugar still present could not now be carried out according to my plan, on account of the treatment with the ether.

The reducing power of the extract in the original beer was 29.87; but after the removal of the antiseptic and subsequent fermentation, only 22.27. If one calls the true maltose in 100 parts of the extract  $x$ , 100 extract after fermentation gives  $(100 - x)$  extract with  $(29.87 - x)$  apparent maltose. Expressed in per cent. of the extract left after fermentation, this value is 22.27, consequently:

$$\frac{100 (29.87 - x)}{100 - x} = 22.27.$$

The beer extract therefore contained 9.78 per cent. of real maltose, and the beer itself .44 per cent.

Now unless the most scrupulous care had been observed during the manufacturing, this beer could not be supposed to keep well. I think it as well not to mention the nature of the preservative, as this would only advertise it; but I hope I have given an easy process to distinguish genuine beers from adulterated ones.

## QUANTITATIVE ESTIMATION OF NITRIC-NITROGEN.\*

By DR. E. FRICKE.

SINCE analytical and manufacturing chemists have agreed to estimate the nitrogen in saltpetre directly, and no longer from the loss, a host of processes have been proposed which are said to answer the purpose, besides being expeditious. In the meeting of the directors of the German Agricultural Stations, held in September, 1888, in Bonn, Jodlbaur's process was recommended. This process, however, gives according to our, and other

\* *Zeitschr. f. Angew. Chemie.* April, 1891. (Slightly abridged.)

analysts' experiences, only good results when the greatest care is exercised, and takes up rather too much time, so a more easy method is preferred.

Förster's process is based on the same principle, and gives very good results indeed. Both methods, however, suffer from the drawback that the analyst is supposed to work on about .5 gram. of the sample, which makes it exceedingly difficult to get a good average portion. A process which we used some years with the best success was originally proposed by Lievert. It is as follows:—20 grams. of the sample are dissolved in a litre of water, and of this solution 50 c.c. are put into a 600 c.c. flask, diluted with an equal bulk of water, and 20 grams. of caustic potash are added. After this has dissolved, 75 c.c. of spirits of wine are mixed with it, and further 15 grams. of zinc and iron powder. To prevent frothing a few granules of animal charcoal may be added. The flask is now closed, and connected with a 200 c.c. Peligot's tube, which contains 10 c.c. of normal sulphuric acid, and is partially immersed in cold water. After three or four hours the spirit, which of course carries over the ammonia, is distilled off by heating with a very small flame, the operation lasting about two hours, when all the alcohol will have distilled over. The acid is then titrated back with  $\frac{7}{8}$  soda. This method is really an excellent one providing the potash is free from nitrates, and the zinc and iron dust are not too much oxidised. The reduction by means of aluminium wire, proposed by Stutzer, is not to be recommended, as everything depends on the nature of the metal. The pure metal now-a-days prepared by electrolysis, is far less active than the metal prepared according to the old process, which gives a product containing sodium and silicon.

Schmitt has lately proposed a method based on the reduction of nitric acid by nascent hydrogen in acid solutions. 40 c.c. of glacial acetic acid are put into a 600 c.c. flask containing 15 grams. of the zinc iron mixture. 50 c.c. of the saltpetre solution are now added, and when the evolution of hydrogen has somewhat ceased, another 15 grams. of the metal are added, and if the mass should get pasty, about 30 c.c. of water. The reduction is completed in about forty minutes; soda ley is added until the zinc hydrate has redissolved, and the ammonia is then distilled off.

This method gives thoroughly good results if one succeeds in preventing frothing, and the spurting over of any alkali. All these processes (which give excellent results in skilful hands) must, however, make room for the method lately proposed by Ulsch, which also is based on the reduction of the nitric in acid solution. This process is characterised by simplicity, celerity, and economy, and according to my experiments with pure nitre, it yields remarkably good and concordant results. According to Ulsch's directions, 25 c.c. of a solution containing about .5 gram. of nitre or .4 gram. of Chilian nitre, are put into a 600 c.c. flask, and reduced by means of 5 grams. of reduced iron and 10 c.c. of dilute sulphuric acid (1 vol. acid + 2 vols. of water). The flask must be covered with a pear-shaped piece of glass to prevent loss by spurting, owing to the violent evolution of hydrogen. When the action somewhat ceases, the reduction must be accelerated by the gradual application of heat until finally the liquid has boiled for about six minutes. After diluting with about 150 c.c. of water, 30 c.c. of soda ley of 1.25 sp. gr. are added, and after introducing a few pieces of granulated zinc, the ammonia is distilled off as usual.

On trying this process on a sample of chemically pure nitrate of soda, we found 16.44 instead of 16.47 per cent. of nitrogen.

When nitric acid has to be estimated in potable waters, we have always used the reduction process in a alkaline fluid; but we felt anxious to know whether Ulsch's process would answer in this case. We found that if one litre of water is evaporated down to about 50 c.c., best after addition of a few drops of soda ley, the resulting fluid may be very accurately treated according to Ulsch's directions.

### LAW NOTES.

#### IMPORTANT DECISION AS TO LIABILITY OF MILK CARRIERS.

HOTCHIN, APPELLANT—HINDMARCH, RESPONDENT.

THIS CASE, an appeal from justices at South Shields, raised the important question whether a milkman or other servant can be convicted under the Adulteration Act of selling milk or any other article adulterated which he sells on behalf of his employer. Hotchin, a milkman, had been convicted under section 6 of the Adulteration Act, 1875, for that he had sold to the respondent Hindmarch three gills of milk "not of the nature, substance, and quality of the article demanded by the purchaser." It was proved and found as a fact that Hindmarch, who is sanitary inspector of the urban sanitary authority of the borough of South Shields, met Hotchin with a cart, vending milk. The cart had upon it the name of "The Farmers' and Cleveland Dairy Co. (Limited)." Hindmarch asked of him three gills of milk, which the man sold to him for 3d. The proper steps were then taken to have it analysed (Hindmarch telling him he had bought it for the purpose), and the analyst certified that it contained 12 per cent. of added water. Hotchin told the inspector at the time that he was selling the milk for the company, in whose service he was foreman. It was objected that the company was the sellers, but this the justices overruled. The defendant relied on section 25 of 38 and 39 Vict., c. 63, on the ground that the milk was purchased by the company with a written warranty that it was genuine milk, and that neither he nor the company had any reason to believe it was otherwise, and evidence was given for the defence thus suggested. A railway clerk stated that two cans of milk, on the morning of the sale, came to the station consigned to the company by some one at Dumfries, each can having a label on it stating the date and quantity of milk it contained (which was found to be correct), and they were received for the company. The witness, however, stated that there was no protection against the milk being tampered with *en route* in a distance of about ninety miles. Each can was labelled—"34 imperial gallons of warranted genuine new milk with all its cream on, from R. Thompson, Dumfries, to the Farmers' and Cleveland Dairy Company, High Shields." One of the company's men stated that he had received the two cans, the contents of which were apportioned between Hotchin and another man for sale. He did not, however, test the milk when received or did he ever test it, and that though Hotchin often tested the milk with a lactometer, he did not do so on the morning in question, for what reason the witness did not know. Hotchin himself was called as a witness, and stated that he was a local foreman of the company, and had a shop where he sold the milk; that he received the milk on the morning in question and sold it exactly as he received it, and he said he sold it for the company. He admitted that he had the means of testing the milk, but did not do so, and could give no reason why he did not do so on this occasion. The written contract between Thompson and the company was produced, and he agreed to supply them for a period from October, 1890, to March, 1891, "with the whole of his dairy of genuine good new milk, of the best quality, with all its cream on," and he thereby "warranted each and every supply of milk delivered under the contract to be pure genuine new milk, unadulterated, with all its cream on." But evidence was given that the district manager had stated at the office of the inspector that he had known five days before that there was "something wrong with the milk," and that it was supposed to be watered, which, however, he denied. On the whole of the evidence the magistrates convicted the accused, but stated a case, in which they stated that it was contended—(1) that he was not the seller; and (2) that section 25 of the Act exempted him from liability on the ground that he believed that the milk sold was that sent. But the magistrates found that he had no reason to believe this under the circumstances.

Mr. Mansfield appeared for the milkman, the appellant, and urged that he ought not to have been convicted.

Mr. Chitty appeared for the prosecutor in support of the conviction.

Lord Coleridge, in giving judgment yesterday, said the case had been very ingeniously argued and, in consequence of another decision, not quite easy of determination. But he had come clearly to the conclusion that the conviction ought to be upheld. The Adulteration Act was directed against adulteration, and pointed to particular acts done by particular persons, one of which was selling the adulterated article. The intention or quality of the act pointed at was for the magistrate to ascertain and determine. But the act itself in every case was at all events a physical act which the party must know he is doing; and if it was outside the proviso for protection he was liable to be convicted, even though he was a servant. The 6th section was that no person shall sell an article which is adulterated. If a person did so he was liable to the penalty, unless he became within any exception of the proviso.

If he, in fact, sold an article adulterated then he was liable to be convicted even though he was a servant. The question had been raised what was "selling" within the Act. In several sections it appeared that selling meant the physical act of transfer of the article, and that the person was liable who did such act. Under the 25th section, however, there would be a defence if the seller showed that he purchased the article as pure and sold it as he purchased it; and it was urged that the seller must mean the purchaser of the commodity afterwards to be sold. That was an ingenious argument, but if it were admitted the Act might just as well not have been passed, and a fraudulent dealer had only to make such a contract, and neither he nor the actual seller would be liable, however much the article might be adulterated. He could not, therefore, yield to the argument (though it had at one time been accepted valid in cases of contracts), for if it were admitted it would make the Act entirely nugatory. It was urged, however, that in the case cited the Court so held, but in truth it had not so held, for it was held on a different state of facts. In that case there was a finding of fact that the contract was *bona fide*, and that the milk had been sold under it, without being altered. And upon that finding the judgment was quite right. It was not so in the present case, for the magistrates found that there was nothing to show that the milk sold was the milk sent under the contract, and, in fact, there was a transit of ninety miles during which the milk might have been tampered with; and, further, it appeared that the milkman might have tested the milk and had not done so. Even, therefore, if the 25th section applied—and he thought it did not apply—the case did not raise a defence under that section, and the case cited did not apply. The conviction, therefore, was right and must be confirmed.

Mr. Justice Mathew concurred. It was clear, he said, that in point of fact the milk sold was adulterated, and the defendant, the milkman, sold the milk so adulterated. The offence was, in the terms of the Act, that he did sell milk which was adulterated, and that offence he had committed. The Act did not except servants; and if they had been excepted it would have been of little avail. The Legislature it was clear meant to deal with the person who actually sold, and if he were not liable then, though he had himself adulterated the article, he could not be convicted and his innocent employer would be liable. He agreed that section 25 raised in this case no defence for the accused. The conviction, therefore, was right.

Appeal dismissed.—*Times*.

### CORRESPONDENCE.

[The Editor is not in any way responsible for opinions expressed by his correspondents.]

To the Editor of the ANALYST.

#### EFFECTS OF FROST ON WATER ANALYSIS.

SIR,—Having obtained some curious results during the frost of last winter, I should be much obliged if any of the members of the Society of Public Analysts would give me their opinion on them, and also if any of them could inform me where information on this subject can be obtained, for, although I have read almost everything that has been written on the subject of water analysis, I cannot find anything specially bearing on this point.

The water in question is a public water supply obtained from a river, and at ordinary times the following is about its average composition:—

| In parts per 100,000           |     |     |     |        |
|--------------------------------|-----|-----|-----|--------|
| Free Ammonia                   | ... | ... | ... | 0.001  |
| Albuminoid Ammonia             | ... | ... | ... | 0.006  |
| Nitrogen as nitrates, etc.     | ... | ... | ... | ...    |
| Nitrites                       | ... | ... | ... | 0.039  |
| Chlorine                       | ... | ... | ... | 1.500  |
| Total solid matter in solution | ... | ... | ... | 12.500 |

During the frost of the last winter the river was frozen for about a month, and during this period the following is about the average of the results:—

|                                |     |     |     |        |
|--------------------------------|-----|-----|-----|--------|
| Free Ammonia                   | ... | ... | ... | 0.009  |
| Albuminoid Ammonia             | ... | ... | ... | 0.010  |
| Nitrogen as nitrates, etc.     | ... | ... | ... | ...    |
| Nitrites                       | ... | ... | ... | 0.098  |
| Chlorine                       | ... | ... | ... | 2.400  |
| Total solid matter in solution | ... | ... | ... | 22.000 |

Can this large variation in the results be accounted for by the effect of frost alone, and what opinion should be given on such a water; and again, what allowance, if any, should be given for the effect of frost in judging the quality of a water from the result of an analysis? I cannot find that these questions have ever been discussed, but if so I will be very much obliged if any of your readers will let me know where the information can be found.

I am, yours truly,

Chester.

May, 1891.

W. F. LOWE,

Analyst for the Counties of Flint, Carnarvon, Denbigh, etc.

ERRATA.—In May number, page 98, line 24, for 15.3 read 18.3; and page 99, line 10, for cooled read cooling.

# THE ANALYST.

JULY, 1891.

## EDITORIAL.

As already announced in the June number of *THE ANALYST*, the Society of Public Analysts have re-acquired from the late Editor and Proprietor the copyright of the Journal.

The Council of the Society cannot let this event pass by without placing on record the deep obligation which the Society is under to Dr. John Muter, who for many years past has undertaken—at first in conjunction with the late Mr. W. G. Wigner, and afterwards unassisted—the arduous labour of editing *THE ANALYST*, to the immense advantage of the Society and of the profession of analytical chemistry. The Society has, at the same time felt that it should, as soon as its financial condition permitted, acquire the absolute ownership of the Journal. This time has at length arrived.

*THE ANALYST* is the oldest journal in any language devoted to the analysis of food. In course of time, its scope has been widened, and it is, at present, the only scientific periodical in England exclusively devoted to the publication of the results of analytical research. It has been of incalculable educational value, not only to public analysts, but to analytical chemists generally.

That *THE ANALYST* is susceptible of much improvement both in its outward appearance and its contents, especially as regards the abstracts on analytical subjects, cannot be gainsaid. Since the Society acquires the Journal in the middle of a volume, it is obviously debarred for the next few months from making any great alterations; but in taking the management into their hands, the Council have the full determination to make *THE ANALYST* worthy of that important section of the profession whose interests it represents.

In this desire the Council rely upon the cordial co-operation of the subscribers, contributions being invited from all analytical workers, with the promise of prompt and wide circulation, strict impartiality, and resolute avoidance of personalities.

Following a rapidly extending practice, the Council have decided to entrust the publication of *THE ANALYST* to an Editorial Committee, who will be assisted by Abstractors of special experience.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A GENERAL meeting of the Society was held on the 3rd ult., at Burlington House, the President, Mr. Hehner, in the chair.

The minutes of the previous meeting were read and confirmed.

A ballot was taken for new members, and the following were declared elected:

As member, J. Rymer Paterson, B.Sc., Analyst, Edinburgh.

As associate, B. H. Gerrans, assistant to Mr. Cassal.

The following papers were read and discussed:—

“On the Action of Milk Preservatives,” by A. W. Stokes.

“Experiments on the influence of Boric Acid on Peptic Digestion,” by the President.

“Experiments on the Estimation of Boric Acid,” by the President.

‘Note on the Composition of Butter-fat,’ by A. H. Allen.

“Fat-free Paper for use in Milk Analysis,” by Dr. P. Vieth.

The President said that those gentlemen who had received *THE ANALYST* that day would have seen that a new era had commenced with the Society. That journal,

which for many years had been in private hands, had now become the property of the Society, and would in future be carried on by the Council. That such a change was not only desirable, but necessary, must have been evident to all those who had watched *THE ANALYST* during the last few years. They, as a Society, owed a debt of gratitude to Dr. Muter, who had carried them over a time of difficulty. As mentioned in the manifesto he had published, Dr. Muter took over *THE ANALYST*, and carried it on at a time when, had he not done so, it was possible that both the Journal and the Society might have come to grief. The Society stood now in a different position, and they could look upon their future with confidence. It was determined to take *THE ANALYST* over on the first opportunity, and they had done so that day. They firmly relied upon every member of the Society, perhaps even more than in the past, to assist in filling the pages of their journal with matter which would be, not only worthy of the Society, but would also be honoured and quoted by men of science all over the world.

The summer meeting of the Society, with which it is proposed to combine an excursion into the adjacent country, will be held this year in London. Full particulars will be announced in due course.

### THE INFLUENCE OF MILK PRESERVATIVES.

By MR. A. W. STOKES.

*(Read at Meeting, June 3rd, 1891.)*

DURING about a year I have been interested in determining the acidity of milk as influenced by temperature and by the addition of preservatives. Between four and five hundred determinations of acidity have been made for that purpose under various conditions. Though there is much more remaining that might be done to complete the enquiry the results so far obtained may be of interest.

Milk as delivered to the London trade is always acid, this acidity on an average is equal to 0.2 per cent. of lactic acid. Such an amount of acidity usually develops in the milk within eight hours of its coming from the cow.

In England, according to the temperature, in from 30 to 40 hours after it has reached an acidity of 0.2 per cent., its acidity rises to 0.35 or 0.4 per cent., at which point it has acquired an acid taste, and is said to be sour.

Usually at an acidity of 0.6 to 0.7 per cent. it separates or coagulates.

If kept for a long period milk rarely develops a greater quantity of lactic acid than 2 per cent. In some milk, the acidity of which I determined (see *ANALYST*, xii., 226), the highest acidity found was 2.34 per cent. after 117 days of keeping. The reason of this is, that when this amount of acidity is reached the acid formed is destructive to the fungus forming it. Milk that has not yet developed an acidity of 0.3 per cent., but is near it, will coagulate on boiling; it is therefore customary in the trade to test the freshness of a milk, if it is suspected to be stale, by boiling it.

To find how long a milk, not sealed up, will keep fresh, without becoming at all sour to the taste, I took a large quantity of the same milk and divided it into 11 parts; one part was kept in its original state, another part was boiled, and to the others various preservatives were added. All these were placed in separate bottles, which were kept open; at intervals of about four hours their acidity was determined.

They were shaken each time that the acidity was determined.

The time was noted when each became sour.

Taking the moment when the unpreserved milk became sour as the starting point I find that the others kept fresh to the following extent longer :—

Samples containing one part per 1,000 of a mixture of equal parts of (dry) carbonates of soda and potash kept fresh five hours longer and became sour to the taste at an average acidity of 0.32 per cent. lactic acid.

Samples containing two parts per 1,000 of the above mixture kept fresh for twenty hours longer and tasted sour at an average acidity of 0.45 per cent.

Samples boiled kept fresh twenty hours longer than the ordinary milk and tasted sour at 0.32 per cent. acid.

Samples containing 10 per cent. of a saturated aqueous solution of salicylic acid kept fresh twenty hours longer, tasting sour at about 0.44 per cent. acid.

Samples containing one part per 1,000 of borax (crystal) kept fresh for seventeen hours longer, tasting sour at about 0.4 per cent. of acid.

Samples containing two parts per 1,000 of borax, kept fresh for twenty-five hours longer, tasting sour at about 0.12 per cent. of acid.

Samples containing one part per 1,000 of boracic acid kept fresh for twenty-four hours longer, tasting sour at about 0.44 per cent. of acid.

Samples containing two parts per 1,000 of boracic acid kept fresh for forty-two hours longer, tasting sour at about 0.46 per cent. of acid.

Samples containing one part per 1,000 of a mixture of equal parts of borax and boracic acid kept fresh for twenty hours longer, tasting sour at about 0.42 per cent of acid.

Samples containing two parts per 1,000 of above mixture kept fresh twenty-seven hours longer, tasting sour at about 0.49 per cent. of acid.

The average temperature was 65° F.

The usual proportion recommended by the vendors of preservatives (almost all of which are, in my experience, composed of borax or boracic acid, or mixtures of the two) is about one part to 1,000 of the milk.

Salicylic acid is too insoluble to make it possible to use much of it; personally, I have never found it in milk.

From these experiments I find that boracic acid is the best preservative. Whatever the preservative, the milk tastes sour when it reaches about the same acidity 0.4 per cent. to 0.49 per cent.

Though the addition of carbonates of soda and potash or borax reduces the original acidity of the milk, and should therefore apparently give it a longer range and time before it reaches the acidity at which it must turn sour, and while on the other hand boracic acid adds to the original acidity and so apparently lessens the range and time, yet the action is reversed and boracic acid is the best preservative.

How great the apparent difference is may be noted from an instance: a sample of milk had an acidity of 0.15 per cent.

On adding two parts per 1,000 of borax its acidity sank to 0.11 per cent.



While that to which two parts per 1,000 of boracic acid was added had an acidity of 0.23 per cent.

Boiling the milk seems as efficacious as the use of one part per 1,000 of any the preservatives.

Four years ago I endeavoured to find the limit at which borax could be detected by the turmeric reaction in milk.

I found that a drop of milk containing the thousandth of a grain of borax would give the reaction if treated thus:—On a porcelain slab place one drop of the milk with two drops of strong HCl and two drops of a saturated turmeric tincture. Dry this on the water bath, take it off directly it is dry. Cool. Add a drop of ammonia by means of a glass rod. A slatey-blue colour changing to green is produced. Even less than this will give the green tint, but not the blue. The turmeric tincture must be fresh, otherwise it is better to use the powdered turmeric.

Even half this quantity of boracic acid can thus be detected; in such case the HCl should be omitted from the test.

Though unpreserved milk usually turns sour to the taste when its acidity reaches 0.3 per cent. there are yet exceptions. I found three samples which, when they reached me they were quite fresh to the taste, though having an acidity of 0.5 per cent. In forty-seven hours later they were of an acidity of 0.51 per cent. At this stage I took parts of each and boiled them without their coagulating at all. Only at the 71st hour, when their acidity was 0.65 per cent., did they become at all sour to the taste. Such exceptions show that milk does not always decompose at the same rate as is asserted in some quarters.

To Mr. W. N. Yarrow I am greatly indebted for care and attention in carrying out much of this tedious enquiry.

The acidity in the above cases was determined by means of decinormal soda solution, using phenol-phthalein as an indicator.

Being asked some time ago to devise some method simpler than the burette for rapidly determining the acidity of milk for use in the milk trade, I had made some compressed pellets containing carbonate of soda and phenol-phthalein. By modern automatic machinery it is possible to weigh out successive quantities of as little as two tenths of a grain with great accuracy. So that, compressed into little pellets of  $\frac{1}{8}$  inch diameter and weighing only one grain each, we have accurate quantities of the alkali and the indicator. Into a narrow tube milk is poured up to a 10 c.c. mark, a pellet is dropped into this milk and crushed by a glass rod. If a permanent pink colour is not produced other pellets are dropped in until the pink colour is permanent. The number of pellets used gives in tenths of a per cent. of lactic acid, the acidity of the milk. The accuracy of the method within the range of acidity in milk and within the limits of one-tenth of a per cent. have been vouched for by several analysts.

The principle of these pellets, that is, the use of accurate quantities of dry compressed reagents, may be useful in other branches of science—hence I may be excused for mentioning the subject.

#### DISCUSSION.

MR. CASSAL said that the use of boric acid and of other antiseptic agents for the preservation of food was a subject which required immediate and full discussion by

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public analysts. Inasmuch as refrigeration when properly applied was a legitimate method of preserving milk, it would be interesting to know how long decomposition could be retarded by it under normal conditions. He did not gather that Mr. Stokes had made any experiments in this direction. He had reason to believe that refrigeration was found to be amply sufficient for all practical purposes, when it was deemed necessary to adopt precautions against premature decomposition. With regard to the tumeric test, evaporation on porcelain had already been mentioned at the Society as a useful modification of the application of this test. He understood that Mr. Stokes approved of this modification for the detection of minute quantities of boric acid. With regard to the acidity pellets, he (Mr. Cassal) was bound to say that he regarded with strong disfavour the introduction of all devices, which were calculated to make untrained persons of various degrees of ignorance imagine that they could act as their own analysts or consulting chemists. It was highly undesirable to put these "tests" into the hands of dairymen and others. They were edge tools likely to wound unskilled hands; while, from a professional point of view, it was objectionable also. As it was, the public, in their ignorance, were far too ready to believe that the whole of the work of analytical chemists consisted in the application of "tests" of this kind. He submitted that, in any case, such a step should only be taken after consultation, and with the general approval of the profession.

DR. VIETH said he supposed Mr. Stokes had made his experiments during the winter months, and he was quite sure that if they were repeated during the summer or autumn the results would be very different. The temperature of the room in which they were made was not the only factor to be taken into account. There was no doubt milk went sour much more quickly in summer and autumn, October and November being the most troublesome months. Farmers attributed this to the decaying leaves, and this was perhaps not far from the truth. He was rather surprised to see that the milk kept for about 170 days had contained 2·3 per cent. of lactic acid; his own experience was, that as soon as 1 to 1·5 per cent. was reached, fermentation practically ceased, or at any rate proceeded with extreme slowness. With reference to the retarding action of boracic acid on lactic fermentation, other experimenters had not got such good results as Mr. Stokes. His impression was that Mr. Stokes had made his experiments at a time most favourable for showing the best action of the preservative. As far as the milk trade of London was concerned, he most emphatically repeated what he had said on former occasions, viz., that in his opinion there was no reason whatever for using any preservative. Dr. Vieth added, that in cheese making it was a necessity that the milk should have a certain degree of acidity. During the last four years a number of tests had been introduced for determining the acidity of milk, and he thought that Mr. Stokes' was the most simple, handy and reliable that could be placed in the hands of the practical cheese maker.

THE PRESIDENT said, that if allowance was made for the content of inert matter in borax, its activity was as near as possible the same as that of boric acid; this was shown by Mr. Stokes' experiments. As to hydrofluoric acid, his experience was that it kept milk samples perfectly for a great length of time.

In reply, Mr. Stokes said that the mass of milks referred to were analysed from January to May last. In reference to Mr. Cassal's objection to his supplying the milk trade with an apparatus that could be readily and cheaply used for stopping the sale of stale milk, he really thought such an apparatus would be an advantage to all parties. Acidity must be determined at the moment the milk is suspected. It would be impossible to send such samples to professional analysts, since, in the majority of cases, the milk would have so far changed in its passage to the analyst as to make an acidity determina-

tion then of very little value. He thanked Dr. Vieth for his generous testimony to the accuracy and simplicity of the pellet method referred to. If it only prevented, to some extent, stale samples being sent for analysis, it would save much trouble and not a few ambiguous results. Mr. Stokes certainly objected to milk being "preserved" by any other means than refrigeration or scalding.

## ON THE INFLUENCE OF BORIC ACID ON PEPTIC DIGESTION.

BY OTTO HEHNER.

(Read at Meeting, June 3rd, 1891.)

IN view of the extending use of boric acid and several of its compounds for the preservation of food, precise information as to its action upon the animal body is exceedingly desirable.

While Leffman and Beam (ANALYST, Vol. xiii., p. 103) have found that boric acid has practically no influence on the diastatic action of malt extract, and, presumably, also upon that of the saliva, Gorup-Besanez (*Lehrbuch Physiol: Chemie*, p. 45), a high authority, states that a solution of borax, whilst without influence upon organised ferments, renders non-organised ones inactive.

In order to put these conflicting statements to the test, as regards pepsine, I charged twelve bottles each with 50 grms. of hard-boiled white of egg, which had been rubbed through a very fine sieve, added 250 c.c. of water, containing 0.15 per cent. of hydrochloric acid and 0.34 grms. of pepsine, which had been previously ascertained to be capable of completely dissolving 2,500 times its weight of albumen, in about five hours, at a temperature of 40° C.; 0.033 grms. of pepsine were, therefore, capable of dissolving completely 82.5 grms. of albumen.

To bottle No. 1 no further addition was made; to the other eleven the following quantities of pure boric acid were added: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, and 3.0 grms. The whole of the bottles were then plunged into a water bath and kept at a temperature of 40° C., with frequent shaking.

The albumen dissolved equally well in the whole of the bottles, and after about five hours, solution was complete in all the samples. There was no difference whatever between the action of pure pepsine and that charged with as much as 3 grms. of boric acid. I conclude that boric acid, even in the amounts used, has no retarding influence upon peptic digestion.

## DISCUSSION.

Mr. CASSAL said that Mr. Hehner's experiments were of great interest and importance. They certainly seemed to show that boric acid had no influence on peptic digestion—at any rate outside the body. But it could not, of course, be assumed that boric acid, even in very minute amount, would not injuriously affect the processes of digestion and assimilation in the body. In the experiments with pepsin and albumen, they were not dealing with living tissue or vital processes; and Mr. Hehner had obviously no intention of drawing any other conclusions from his experiments than that the dissolving of egg-albumen by pepsin in a glass vessel, under the usual conditions, was not interfered with by the presence of boric acid. The actual effects of small doses of boric acid required further study; the results hitherto recorded, such as those of Förster, went to show that injurious effects were produced, as indeed on a priori ground it would be reasonable to expect. But apart from this question of injuriousness

it was necessary that public analysts should arrive at a clear understanding and agreement as to how the presence of boric acid in articles of food was to be regarded by them. Was it an adulterant within the meaning of the Act? For his own part, he was unable to see how any public analyst could conscientiously arrive at the conclusion that it was not.

Mr. HENNER, in reply, said that he had not in any way altered the opinion which he had expressed on a previous occasion. He objected to the indiscriminate use of chemical food preservatives, as they were bound to have generally biological action. The experiments which he had brought forward that night showed that boric acid, at least, had no influence upon gastric digestion; but they did not in any way show that boric acid was a desirable ingredient in food. He had lately had to analyse some hams, which had been alleged to have produced injurious effects, and he had found them to be strongly impregnated with boric acid. He had since ascertained that bacon was very largely borated. He was convinced that the dealers in food, who were responsible for the employment of antiseptics, would not knowingly use anything injurious; but it was the duty of public analysts to probe this matter to the bottom, the more so as, sooner or later, it would have to be decided either in a court of law or subjected to legislation.

#### FAT-FREE PAPER FOR USE IN MILK ANALYSIS.

BY DR. P. VIETH.

(*Read at Meeting, June 3rd, 1891.*)

In a paper read before this society in May, 1889 (*THE ANALYST*, 1889, Vol. XIV., p. 121), Mr. Richmond stated that Messrs. Schleicher and Schüll were placing on the market a fat-free paper suitable for fat determinations in milk. For this paper we have had to wait a long time; but it has made its appearance at last, and I thought members might like to know that the paper can now be had of the well-known firm of Townson and Mercer. In a circular the manufacturers state that, "After considerable trouble and many disappointments, we have been successful in manufacturing a fat-free paper by systematically treating it with absolute alcohol. The new article thus produced contains such a slight trace of fat that it has no influence whatever on the analysis."

As soon as I had heard of the existence of the paper, I procured some for the purpose of experimenting with it, and with a view of adopting it for future work, in case the experiments should turn out satisfactory. The paper is thicker than that originally recommended by Mr. Adams, and the strips are consequently heavier; as to matter soluble in ether, this is certainly not totally absent.

In three lots of filter paper, such as I was in the habit of using for plaster cartridges, I had found some years ago .232, .161, and .181 per cent. ether extract, and in two lots of blotting paper of the kind recommended by Mr. Adams .297 and .314 per cent. The new paper gave in one experiment .0278 per cent. ether extract, and in another, in which I experimented on strips which had been previously wetted with dilute acetic acid and dried again, .0250 per cent. The latter figure proves that there was nothing of a soapy nature present. The average amount of matter soluble in ether for one strip, weighing six grammes, is .0016, and this quantity would increase the result of a fat determination by .03, provided the same amount, which is extracted in a blank experiment, is also got out after five grammes of milk have been dried on the paper. I am not at all sure that the latter is the case.

Mr. Richmond, in the paper already mentioned, recommends to continue the extraction for three to four hours. My own experiments lead me to believe that extraction is practically completed in a much shorter time. Two samples, one of whole and one of skim milk, when extracted for different lengths of time, gave the following results:—

| Time of Extraction. |    |    |    | Whole Milk. | Skim Milk. |
|---------------------|----|----|----|-------------|------------|
| 1 hour              | .. | .. | .. | 3.48        | .28        |
| 2 hours             | .. | .. | .. | 3.50        | .30        |
| 3 "                 | .. | .. | .. | 3.54        | .28        |
| 4 "                 | .. | .. | .. | —           | .28        |

Experimenting upon six other samples—three of whole and three of skim milk—I noted not only the time, but also the number of siphonings. The experiments were made with a view to find out the shortest time required for extracting the fat. The following results were obtained:—

| Sample No. | No. of Siphonings. | Time occupied.<br>Min. | Fat—Per cent. |
|------------|--------------------|------------------------|---------------|
| I.         | 3                  | 17                     | .28           |
|            | 6                  | 37                     | .24           |
|            | 9                  | 52                     | .28           |
| II.        | 3                  | 19                     | .22           |
|            | 5                  | 41                     | .24           |
|            | 9                  | 59                     | .24           |
| III.       | 3                  | 13                     | .21           |
|            | 6                  | 47                     | .24           |
|            | 9                  | 41                     | .26           |
| IV.        | 3                  | 24                     | 4.18          |
|            | 6                  | 33                     | 4.14          |
|            | 9                  | 51                     | 4.21          |
| V.         | 3                  | 22                     | 3.54          |
|            | 6                  | 46                     | 3.68          |
|            | 9                  | 64                     | 3.68          |
| VI.        | 3                  | 15                     | 2.84          |
|            | 6                  | 41                     | 2.88          |
|            | 9                  | 50                     | 2.90          |

Of these results, those referring to samples III. and VI. are particularly noteworthy, where with three siphonings, and in the short time of thirteen and fifteen minutes respectively, practically the whole of the fat had been extracted. Although

perhaps of little practical value, this observation is not without some interest. Continuing the extraction for an hour appears to be more than sufficient for all practical purposes.

### THE SEPARATION OF TITANIUM, CHROMIUM, ALUMINIUM, IRON, BARIUM AND PHOSPHORIC ACID IN ROCK ANALYSIS.

BY THOMAS M. CHATARD.\*

HAVING to examine some magnesian silicate rocks containing, in addition to iron and aluminum, small quantities of titanium, chromium, barium and phosphoric acid, the methods for the decomposition of such rocks and the separation of their constituents were studied and compared so as to determine the most advisable manner of procedure. After repeated trials the following course, combining a number of well-known methods, has been found to be the most satisfactory.

The silica and bases are determined by the ordinary sodium carbonate fusion method, in which the hydrates of titanium, chromium, iron and aluminum, together with the phosphoric acid, are precipitated together, and, after weighing, fused with sodium bisulphate, dissolved, the small amount of silica separated, and the solution, after reduction of the ferric oxide, titrated for total iron.

To separate these oxides and at the same time to determine the barium, two grams. of the finely pulverised mineral are put into a platinum crucible or dish, moistened with water, dilute sulphuric acid (1:1) and pure strong hydrofluoric acid added in considerable excess, the vessel put on a radiator to evaporate, and stirred from time to time. When the solution is so far evaporated that fumes of sulphuric acid begin to come off, there should still be so much acid present as to form a solution or emulsion and not a paste, since the paste is liable to bake on the bottom of the vessel and form the difficulty-soluble anhydrous sulphates produced by overheating, especially when magnesia is present in quantity. At this point it is well to add a few drops of nitric acid to oxidise the ferrous oxide, and a little more hydrofluoric acid to insure the complete expulsion of the silica. The evaporation is then continued until the sulphuric acid fumes strongly and no odour of hydrofluoric acid can be detected when the solution is cooled below the point at which the sulphuric acid fumes.

About 25 c.c. of dilute hydrochloric acid (1:5) is now added, the stirring being continued, and the material is then evaporated on the water-bath until most of the hydrochloric acid has been driven off. The material is then washed into a beaker, and any residue adhering to the vessel can be removed by a few drops of hot, strong hydrochloric acid, the vessel being rubbed with a bit of paper if necessary. If the solution be very turbid it can be digested on the water-bath for some time, but ultimately it is diluted with hot water to 250-300 c.c., allowed to stand for several hours, and then filtered.

The residue contains the barium as sulphate, and sometimes small amounts of chromite or other minerals of the same class. It is washed, ignited and thoroughly fused with sodium carbonate in a small crucible, the fused mass being then digested with hot water. The well-washed residue is dissolved on the filter with dilute

\* *Journ. Am. Chem. Socy.* Vol. XIII. No. 2.

hydrochloric acid, and this solution filtered through the same filter, which, after washing, is burned, the ash fused with a little sodium carbonate, the mass dissolved in dilute hydrochloric acid and added to the washings, which are now acidified and added to the main solution, after reduction of the chromic acid. The hydrochloric acid solution containing the barium is evaporated to a few drops to get rid of the excess of acid, diluted, the barium precipitated, and the filtrate from the barium sulphate added to the main solution.

This main solution, which should be perfectly clear and contain the iron and chromium as sesquioxides, is now made alkaline by ammonia, and the precipitate redissolved by dilute hydrochloric acid. A few drops of acetic acid are added, the liquid brought to a boil, ammonia added in very light excess, the boiling continued for a few minutes and the precipitate filtered and washed. As the sole reason for this precipitation is to get rid of the magnesia and the accumulation of other salts, the washing need not be thorough, but the filtrate must be tested and the precipitation proved complete.

The precipitate is dissolved in hot dilute hydrochloric acid. The filter after washing is burned in a large platinum crucible, into which the solution, concentrated to a small bulk, is put and evaporated on the water-bath till it becomes pasty. Just enough water is added to dissolve the salts, and then dry sodium carbonate is added in small portions, with continual stirring, till a comparatively dry mass results. This must be carefully done, for if too much soda is added at a time, and each addition is not thoroughly stirred into the mass, the after fusion is apt to be "lumpy" and unsatisfactory.

When a good excess of carbonate has thus been added, the mass is dried and gradually brought to clear fusion, which should be continued for half an hour. If lumps form, which is, however, rarely the case if lime and magnesia are absent and the foregoing directions are followed, they can be broken up by shaking the crucible with a circular motion to detach them from its walls. When the fusion is complete, the mass is spread around the walls of the crucible and slightly cooled. A small quantity of sodium nitrate is now added, the whole rapidly fused and carefully boiled for not more than five minutes; it is then again spread over the crucible and rapidly cooled with a blast of air. The mass is boiled with water till completely disintegrated, and then filtered and washed; repeated tests have shown that the residue which contains the titanium is, when well washed, free from chromium and phosphoric acid.

The washed residue is dissolved in hot dilute hydrochloric acid, the filter burned, the ash fused with sodium bisulphate, dissolved in water and added to the solution. The titanium in this solution is separated by the excellent method of Dr. Gooch,\* all the details as laid down by him being followed. I have, however, found it convenient, after the destruction of the tartaric acid by potassium permanganate, and the clearing of the solution by sulphurous acid, to add ammonia in slight excess, then at once acetic acid in excess, and boil with addition of sulphurous acid. The precipitate of titanium hydrate, mixed with some alumina, is filtered and washed with water containing sulphurous acid and a little acetic acid. It is thus freed from manganese and brought into a small compass, rendering the after work easier. Before the final precipitation of the titanium the platinum generally in the solution should be removed by hydrogen sulphide.

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\* Proc. Am. Acad, 12, 435 seq. (Bull. No. 27, U.S.G.S., p. 16 seq.).

The filtrate containing the chromic and phosphoric acids is heated, and ammonium nitrate cautiously added till no further precipitation of alumina occurs. The precipitation of the alumina phosphate seems to be complete, but some alumina always remains in solution. The precipitate is allowed to settle, the supernatant liquid decanted and the precipitate washed with a solution of ammonium nitrate until the yellow tinge disappears; it is then dissolved in dilute nitric acid, and the phosphoric acid precipitated by molybdate solution.

The filtrate containing the chromic acid is acidified, boiled, neutralised with ammonia, and the chromium precipitated by freshly prepared ammoniac sulphide. The precipitate, after some washing, is dissolved in hot dilute nitric acid, and, after concentration, potassium chlorate is added, the solution boiled, and finally evaporated nearly to dryness to expel the excess of acid. It is then diluted with cold water, and a saturated solution of sodium bicarbonate added in small excess, separating the last traces of alumina. After standing about three hours, the alumina is filtered and washed with moderately dilute solution of bicarbonate. The filtrate is acidified and the chromic acid reduced and precipitated by ammonium sulphide in a platinum dish, filtered, washed, redissolved to get rid of traces of alkali, reprecipitated, and finally weighed as chromic oxide.

This method, due to Baubigny, for the separation of aluminum from chromium is very good and convenient if the solution be free from iron and contain but little alumina. Careful tests have shown that if iron be present some of it always remains in solution, while if there be much alumina it is almost impossible to wash out all the chromate from the bulky precipitate with the cold solution of bicarbonate which must be used. It must also be noted in this connection that a solution of iron and chromium prepared by the Baubigny method was made ammoniacal, and it was proved that while all of the iron was precipitated, this precipitate, even after the most careful washing with hot water, contained chromium.

Although the number of details in this process may seem very great, experience has shown that none of them can be safely neglected for the purpose of shortening the work; if the whole process be carefully followed out, the results are very satisfactory, as shown by the following tests on a typical magnesian rock:—

|          | Percentage $\text{Cr}_2\text{O}_3$ . | $\text{TiO}_2$ . | $\text{BaO}$ . | $\text{P}_2\text{O}_5$ . |
|----------|--------------------------------------|------------------|----------------|--------------------------|
| No. 1,   | ·270                                 | ·46              | ·010           | ·375                     |
| No. 2,   | ·285                                 | ·39              | ·060           | ·385                     |
| No. 3,   | ·317                                 | ·46              | ·055           | ..                       |
| No. 4,   | ·280                                 | ..               | ..             | ..                       |
| Average, | ·288                                 | ·44              | ·052           | ·380                     |

The use of sodium nitrate for the fusions is not absolutely necessary, though one is more sure of complete oxidation if it be employed. In the analysis of chrome ores the best results have been obtained by fusing the finely-pulverised ore with sodium carbonate alone, but keeping it in clear fusion for an hour. The fused mass is treated like an ordinary silicate fusion, the silica after weighing being volatilised by hydrofluoric acid, and the residue, usually small, again fused with sodium carbonate, giving a clear solution in hydrochloric acid.



## ON THE ANALYSIS OF OLD FLOURS.

By M. M. BALLAND AND V. PLANCHON.\*

OLD flour, which has reached the extreme limit of its possible preservation, and has therefore lost its commercial value, has lately been employed in a new traffic which constitutes an actual fraud. By re-passing such an article through the mill with fresh flour, the mixture escapes detection by trade experts, and passes current as genuine new flour. The apparent goodness, when fresh from the mill, rapidly passes off, however, and, in a very short time, the whole becomes stale. M. Balland has recently had occasion to examine several samples of such flour, with the following results: the proportions both of water and ash were normal; while that of the fat was much less, and the acidity much greater, than the usual amount. The first sample, although really the most ancient, had only issued from the mill within three months, while samples Nos. 2 and 3 were also of the same nature, although not quite so bad.

|              |       | Water<br>per cent. | Ash<br>per cent. | Acidity<br>per cent. | Fat,<br>per cent. |
|--------------|-------|--------------------|------------------|----------------------|-------------------|
| Sample No. 1 | .. .. | 13.70              | 1.10             | 0.147                | 0.78              |
| " " 2        | .. .. | 13.82              | 0.32             | 0.069                | 0.94              |
| " " 3        | .. .. | 13.92              | 0.31             | 0.074                | 0.84              |
| New Flour A  | .. .. | 13.16              | 0.36             | 0.039                | 1.22              |
| " " B        | .. .. | 13.20              | 0.76             | 0.049                | 1.74              |
| " " C        | .. .. | 13.96              | 0.38             | 0.049                | 0.76              |

The estimation of the gluten gives excellent indications, being less cohesive than the gluten of fresh flours.

If it be extracted in the usual manner, and then left under water for twenty-four hours, and if, at the expiration of that time, the washing and squeezing between the fingers be resumed, it froths and loses much of its weight. The following table will show the difference in this respect between genuine young flours and the mixtures now under consideration:—

|              |       | Original gluten<br>per cent. | Gluten, after twenty-four<br>hours in water, per cent. |
|--------------|-------|------------------------------|--|
| Sample No. 1 | .. .. | 29.6                         | 18.0   |
| " " 2        | .. .. | 36.4                         | 27.2   |
| " " 3        | .. .. | 36.0                         | 26.4   |
| New Flour A  | .. .. | 38.8                         | 31.8   |
| " " B        | .. .. | 36.0                         | 32.4   |
| " " C        | .. .. | 36.0                         | 31.2   |

It is therefore evident that the amounts of acidity and of fat and the behaviour of the gluten permits us to pronounce upon the age of the flour, and also enables us to differentiate between a stale and a good flour even when the former is comparatively freshly made.

M. Planchon has made the following experiments:—After quoting the researches of M. Balland to the effect that the normal acidity of good flour represented in monohydrated sulphuric acid can vary between .015 and .040 per cent., he says "One can well conceive that the precise estimation of such small quantities of acid presents consider-

able difficulties, especially when we consider that the titration is performed in an alcoholic liquor, resulting from the prolonged maceration of several grams only of flour, and with turmeric paper as an indicator. It is true that in following exactly the method of operation described, I have always obtained, when working with good flours, figures comprised within the indicated limits; nevertheless, I believe that these figures, although comparable amongst themselves, do not represent the real acidity, because I have obtained very different results by operating in the following manner:—

“Five grams of flour are gradually mixed with 50 c.c. of cold distilled water; when the mixture is perfectly homogeneous two or three drops of alcoholic solution of phenolphthalein are added, and the whole is titrated with  $\frac{1}{50}$  normal soda solution, such solution being delivered from a delicate burette, and the whole being kept in constant agitation during the titration. The number of c.c. of soda used is multiplied by the coefficient .0245, and the figure so obtained gives, in my opinion, the actual acidity of the flour.

To obtain the exact point of neutrality it is necessary to compare the colour with that of a mixture of five grams, of the same flour with 50 c.c. of water, and the same number of drops of the indicator. The operation is so short that the action of the water and the ferments do not cause the formation of any notable quantity of acid. I have proved that when a mixture of flour and water is allowed to stand the amount of the total acidity does not increase during the first two hours. Here, for example, is the result of the titration of the same flour maintained in contact with water for different periods:—

|                         |    |    |    |    |    | Total Acidity per Cent.<br>( $H_2SO_4$ ). |
|-------------------------|----|----|----|----|----|---|
| Titrated immediately .. | .. | .. | .. | .. | .. | 0.110                                     |
| „ after 1 hour ..       | .. | .. | .. | .. | .. | 0.110                                     |
| „ „ 2 „ ..              | .. | .. | .. | .. | .. | 0.110                                     |
| „ „ 4 „ ..              | .. | .. | .. | .. | .. | 0.113                                     |
| „ „ 7 „ ..              | .. | .. | .. | .. | .. | 0.115                                     |
| „ „ 24 „ ..             | .. | .. | .. | .. | .. | 0.126                                     |
| „ „ 48 „ ..             | .. | .. | .. | .. | .. | 0.145 (manifest decomposition).           |

If the total acidity remains the same for two hours, it is still much larger than the amount of acid that enters into solution, because in measuring the acidity of the liquid separated by filtration from the same mixtures I obtained the following results:—

|                 |    |    |    |    |    | Soluble Acidity per Cent.<br>( $H_2SO_4$ ). |
|-----------------|----|----|----|----|----|---|
| Immediately ..  | .. | .. | .. | .. | .. | 0.0107                                      |
| After 1 hour .. | .. | .. | .. | .. | .. | 0.0225                                      |
| „ 2 „ ..        | .. | .. | .. | .. | .. | 0.0230                                      |
| „ 4 „ ..        | .. | .. | .. | .. | .. | 0.025                                       |
| „ 7 „ ..        | .. | .. | .. | .. | .. | 0.0275                                      |
| „ 24 „ ..       | .. | .. | .. | .. | .. | 0.0425                                      |
| „ 48 „ ..       | .. | .. | .. | .. | .. | 0.083                                       |

Maceration in rectified spirit of the same flour during twenty-four hours showed after filtration the presence of .03 per cent. of acidity soluble therein. We thus see that flour does not give up its total acidity immediately either to water or alcohol,

and that the only true method is to directly apply the alkali to the flour itself, in presence of water. I have tested this method of analysis on eleven samples of fresh flour, and from nine of them which were cylinder ground I have obtained a total acidity varying between  $\cdot 105$  and  $\cdot 122$ . The remaining two flours, which were from ordinary stone mills, showed respectively  $\cdot 119$  and  $\cdot 133$  per cent. of total acidity. I have also had occasion to analyse two samples of flour manifestly damaged and unfit for use in the bakery. In the one case I obtained  $\cdot 16$  and in the other  $\cdot 565$  of total acidity. In both of these cases the estimation of the total acidity furnished exceedingly characteristic results, and I consider this simple operation ought never to be neglected in the examination of flour intended for bread-making.

ON THE ESTIMATION OF NITRIC ACID BY CONVERSION INTO AMMONIA, AND OBSERVATION OF THE DEFICIT OF HYDROGEN. BY K. ULSCH (*Zeitsch. f. Anal. Chem.* Vol. 30, p. 175).—The use of zinc for the reduction of nitric acid brings about a loss of nitrogen, owing to the production of nitrous acid. If, however, metallic iron is taken for the reduction, no nitrites are produced. When the reaction is carried out at a temperature of about  $70^{\circ}$  C. it is completed in less than half an hour. The author operates as follows:—A small flask, provided with a triple-bored rubber cork, through one hole of which passes a tapped funnel tube, through the second and third two glass tubes bent at right angles, one reaching to the bottom of the flask, is connected with a nitrometer. Into the flask are placed 3 grammes of iron powder (*ferrum redactum*), and 20 c.c. of a copper solution containing 100 grammes  $\text{CuSO}_4$  per litre. The contents of the flask are heated gently, until the fluid is no longer blue. The precipitate is then washed with several quantities of warm water. The flask is now closed and connected with the nitrometer; 10 c.c. of normal sulphuric acid are then added through the funnel tube and the flask warmed in the water-bath to  $75^{\circ}$  C. until there is no more evolution of hydrogen. The apparatus is now free from air. Once more 10 c.c. of standard acid are added, and the hydrogen produced is measured after it has cooled down to the ordinary temperature, corrections being of course applied for temperature and pressure. The flask is then emptied by means of the tube going to the bottom of the flask, and the nitrate solution to be examined introduced with 10 c.c. of normal acid. The deficit of hydrogen obtained gives the measure of the quantity of nitrate present. 1.106 c.c. hydrogen corresponds to one milligramme of potassium nitrate. The test experiments given are in every way satisfactory. A single charge of 3 grammes. of iron suffices for 25 determinations, if the amount of nitrate does not exceed 10 milligrammes in each case.

O. II.

A NEW METHOD FOR THE QUANTITATIVE SEPARATION OF MANGANESE AND ZINC. P. JANNASCH AND J. F. MACGREGORY (*Jour. f. prakt. Chem.* [2] 43, 402-406).—Manganese can be completely precipitated as dioxide in an ammoniacal solution by hydrogen dioxide. To ensure the freedom of the precipitate from zinc, when that metal is present, excess of ammonium chloride and ammonia must be employed. The authors experimented with 0.5 grm. of re-crystallised manganese and zinc sulphates respectively, dissolved in 75–100 c.c. of water, following the method here set forth:—The solution is acidified

with hydrochloric acid, and transferred to a 600 c.c. Berlin porcelain dish; there are then added successively at least 100 c.c. of a 15–20 per cent. solution of ammonium chloride, 60–100 c.c. of strong ammonia, and an excess (50–60 c.c.) of hydrogen dioxide, the dish being covered with a clock glass to avoid loss by the spurting which occurs from escape of oxygen when the hydrogen dioxide is in excess. The dish is then heated for 10–15 minutes on the water-bath, the precipitate collected on a filter and washed, first with hot ammonia water, and finally with hot pure water, until the washings leave no residue on evaporation. The precipitate can be burnt in a platinum or porcelain crucible while still wet, and must finally be heated over the blowpipe until constant in weight.

To determine the zinc, the mixed filtrate and washings may be precipitated with ammonium sulphide, the zinc sulphide being re-dissolved and precipitated as carbonate in the usual way. A more rapid method, however, is to evaporate the filtrate and washings, dry the residue at 125–150° for one hour, and ignite it over a piece of asbestos mill-board to expel ammonium salts; the asbestos is to prevent the temperature from rising high enough to volatilize zinc salts, its presence renders it necessary to push the salts down from the sides of the dish into the centre. The ignited residue is dissolved in water containing a little hydrochloric acid, and the zinc precipitated from the hot solution with sodium carbonate in the usual manner.

A. G. B.

THE ESTIMATION OF FAT IN MILK BY MEANS OF THE LACTOCRITE. L. F. WILSON, *Chem. Zeit.*, 1891, 15, 649–656).—The growing importance of dairy products and their production as a definite industrial undertaking, requiring the aid of some means of readily checking the quality of the raw material, milk, both to ascertain its commercial value and to determine in what degree the yield from cows and other milk-giving animals can be improved by breeding, have led to the device of numerous methods for the estimation of the constituent with which the butter-maker is most concerned, viz., the fat. The most expeditious method hitherto proposed is that of De Laval, who in applying the principle of the separators in use on a large scale, to the analytical problem stated above, has given us an instrument, the lactocrite, which appears to attain the desired end more perfectly than any other known means.

The construction and mode of use of the lactocrite are well known to our readers (for a description see the ANALYST, 1887, 130). Its accuracy and ease of working have been testified to by many chemists, and it is now made so that it can be driven by hand instead of power. The chief objection that can be urged against the lactocrite, is that it fails to indicate the presence of any fat whatever in skim milk containing less than about 0·5 per cent. of fat, and that its readings up to 1·5 per cent. require the application of a considerable and varying correction (*cf.* Faber, THE ANALYST, 1887, 130). The cause for this seems to lie not in the construction of the apparatus itself, but in the fact that the mixture of sulphuric acid and glacial acetic acid, which is used to dissolve the casein and allow the separation of the fat, attacks the latter to some extent. By substituting for this a mixture of hydrochloric acid and lactic acid in proportions similar to those of the acids they replace, this difficulty is entirely overcome. The modified process has been patented by the Separator Company of Stockholm. The chemist to this com-

pany, M. Ekenberg, has devised a process for preparing lactic acid, by which it will be so much cheapened that the cost of using the lactocrite under the new conditions will be scarcely greater than it was formerly (for another new process for the preparation of lactic acid see *Journal of the Society of Chemical Industry*, 1891, 312).

The author has compared the indications of the instrument used with the altered acid mixture, with the results given by various analytical processes of repute. A brief description of each method as carried out by him is first given.

#### I. LAVAL'S LACTOCRITE METHOD.

The instrument used was supplied by the Separator Co., and was of the size known as "baby," having places for twelve tubes and driven by hand. The milk and acid were measured by the same pipette, it being, of course, previously rinsed with the liquid about to be measured. In testing whole milk the mixture was kept in the water-bath for eight to ten minutes, while for skim milk six to eight minutes sufficed. The lactocrite was heated to 50-60° C., by means of steam, and the rotation continued for about five minutes at the usual speed of 6,000-7,000 revolutions per minute. Each sample was tested either six or twelve times, the results being usually identically or, in any case, very closely concordant for the same sample. In a few instances a bubble made its appearance in the column of fat in the capillary portion of the lactocrite tube, in which case the experiment was rejected. If an apparatus of somewhat larger size, *e.g.*, one with twenty-four tubes be used and the operator have assistance in washing up, etc., some two dozen tests per hour can be made, so that with two persons familiar with the instrument, and working alternately, 300-400 tests can be carried out in an ordinary working day. It is thus remarkable not only as the first analytical apparatus dependent upon mechanical power, but also results are obtained by it more speedily than by any known analytical process whatever.

#### II. SOXHLET'S AREOMETRIC METHOD.

(*Zeit. Landwirth. Ver. Bay. Munchen*, 1880).

The apparatus used by the author was obtained from J. Greiner, of Munich, and was accompanied by two certificates by the inventor stating that the two hydrometers sent therewith were accurate. When tested against ordinary gravimetric methods for the analysis of whole milk the process was found perfectly satisfactory.

The ethereal fat solution was always brought, in the test experiments, to the normal temperature of 17.5° C., by means of a stream of water of that temperature supplied from a vessel holding about 15 litres kept continuously running through the water-jacket, and thus all correction for temperature was avoided. The ether was purified before use by treatment with calcium chloride and caustic lime, distilled and saturated with water at the ordinary temperature.

No difficulty in separating the ethereal from the aqueous layer was experienced either with whole or skim milks, a circumstance that may have been due to the fact that the samples were fresh.

#### III. GRAVIMETRIC METHODS.

Of the methods that depend on the absorption of the milk by some porous substance, such as sand, pumice-stone, asbestos, cotton, wool, and the like, and the extraction of the fat from the total solids thus finely divided, the author has used the following:—

(a) Pumice-stone, broken and sifted, so as to produce a material of which the particles were 0.5-1.0 mm. in diameter, is washed with water, ignited, and about twelve grms. placed in a porcelain basin. About 12 grms. of milk are then allowed to drop upon it so as to be thoroughly absorbed, dried at 97-98° C., the operation being completed in a vacuum water oven, kept exhausted by a water pump. The residue is transferred to a paper cartridge and extracted with ether in a Soxhlet apparatus in the ordinary way, any particles adhering to the dish being removed by a little more pumice and a plug of pure cotton-wool. The paper cartridge is made of best Swedish filter-paper used double, which has been extracted for at least twelve hours with ether, and thoroughly dried, and is supported on a layer of cotton-wool similarly purified, to retain any fine particles of pumice that may find their way through.

The ether used in extraction is freed from water and alcohol by the method described under (2), supplemented by treatment with sodium until hydrogen ceases to escape, and final distillation.

Good as pumice-stone is, its pores are too large for perfect division of the particles of milk solids, the fat globules remaining encased in casein to some extent, a fact evidenced by the perceptible extra yield of fat obtained by pulverising the pumice, and re-extraction after previous thorough exhaustion.

(b) In pursuance of the principle of J. Lehmann's method, which consists in the use of clay plates as an absorbent, the author has employed powdered, lightly burnt clay vessels, freed from dust by washing with water on a sieve, so as to leave particles about 0.5 to 1.5 mm. in diameter. The process is carried out in the same way as with pumice-stone, save that 22 grms. of the absorbent material are taken instead of 12.

The extraction apparatus used by the author consisted of a battery of four Soxhlet tubes, with flasks and condensers ground in, thus avoiding the use of corks. Each flask was supported by a small porcelain dish containing a little sand, heated by means of a jet of gas from the small inner gas tube of a Bunsen burner, the flame being so placed that one side of the basin was heated and bumping thus avoided. By this arrangement the rate of extraction could be easily regulated, and the syphon of the Soxhlet discharged about every five minutes. In order to prevent the formation of bubbles in the ether collected in the extraction tube, a paper shield was placed round the extractor just above the flask. As the flow of ether out of the double paper cartridge, and through the underlying plug of cotton-wool, is somewhat slow, a little piece of cotton-wool is inserted into the mouth of the syphon, so that the rate at which the extraction tube is emptied is also decreased. The use of a sand-bath instead of a water-bath for the extractor flasks is advantageous, as their weights remain practically constant and they last much better.

Test analyses were made of whole and skim-milk, to ascertain how long the extraction should be continued in order to be complete. It was found that three hours generally sufficed for the extraction of fat from whole milk, but that twelve hours were necessary for skim milk containing about 0.8 per cent. of fat.

(c) The author also examined Adams' process, and quotes the opinions of Klein, Richmond, and others as to its accuracy, mentioning that it tends to yield higher results than the other methods. In his investigations he used Schleicher and Schüll's "fat-

free paper," having first ascertained what quantity of matter soluble in ether was present in it. The amount found was just over 1 m.grm. for each strip, that being the form in which the paper is sold. Extraction of the paper with ether for two hours removes this impurity.

Experiments made to determine the length of time for which extraction had to be continued to dissolve the fat from the milk solids showed that three hours were ample, thus confirming Adams' statement. Nevertheless, the author adopted the period of five hours for whole milk, and twelve hours for skim milk, to avoid possibility of error. He records the fact that of all the methods tried, the Adams' process showed the closest concordances in successive experiments.

The following table shows the mean results of the different methods with various samples of milk :—

| Powdered earthenware. | Lactocrite. | Areometer. | Blotting paper. | Remarks.  |
|-----------------------|-------------|------------|-----------------|---|
| 3.66                  | 3.71        | 3.71       | 3.74            | Morning milk from cow No. 7.  |
| 3.63                  | 3.62        | 3.68       | 3.73            | Morning milk from cow No. 3.  |
| 3.09                  | 3.13        | 3.18       | 3.18            | } Morning milk from several cows.   |
| 3.08                  | 3.10        | —          | —               |   |
| 2.67                  | 2.72        | 2.77       | 2.76            | } Morning milk from cow No. 13.   |
| 2.55                  | 2.52        | 2.56       | 2.60            |   |
| 2.38                  | 2.43        | 2.49       | 2.49            | Morning milk from cow No. 14.   |
| 2.19                  | 2.23        | 2.34       | 2.28            | { Mixture of two parts of hand-skimmed milk, 24 hours old, with one part of morning milk from cow No. 14. |
| 1.35                  | 1.41        | 1.47       | 1.43            |   |
| 0.85                  | 0.90        | 1.02       | 0.94            | Milk, 24 hours old, from several cows.  |
| 0.76                  | 0.82        | 0.91       | 0.86            | } Milk, 48 hours old, from several cows.  |
| —                     | 0.69        | —          | 0.74            |   |
| —                     | 0.42        | —          | 0.48            | } Milk "separated" by hand "separator."   |
| 0.31                  | —           | 0.50       | 0.40            |   |
| —                     | 0.28        | —          | 0.33            | } Milk "separated" by "separator" driven by power.  |

The differences between the three methods that give the best and most concordant results, viz., the Adams process, the powdered earthenware method, and the lactocrite, are as follows :—

|                                       | Maximum. | Minimum. | Mean.  |
|---------------------------------------|----------|----------|--------|
| Between Adams and earthenware .. ..   | +0.11    | +0.05    | +0.088 |
| Between Adams and lactocrite .. ..    | +0.11    | +0.02    | +0.052 |
| Between lactocrite and earthenware .. | +0.06    | —0.03    | +0.035 |

It therefore appears that the lactocrite used with the new solvent mentioned at the beginning of this paper gives thoroughly reliable results with the most diverse kinds of milk.

Soxhlet's areometric method is less accurate than the lactocrite, particularly with skim milks. The reason for the constant tendency of the Adams process to give higher results than any method in which an absorbent other than blotting-paper is used, appears to be due to the interstices of the blotting-paper being so fine that the fat globules fail

to penetrate into them, and remain, therefore, on the surface already largely freed from the milk serum, and consequently are easily dissolved by the ether.

The porous earthenware method gives lower results, because the sample used by the author was not sufficiently close in texture, but this disadvantage he considers in some measure counterbalanced by the facts that no special care is needed to free it previously from matter soluble in ether, and that it can be used repeatedly after mere ignition, the presence of the ash from the milk increasing its powers as an absorbent.

The author supplements the foregoing work with a description of some experiments made by him on the use of kaolin as an absorbent as proposed by Dr. Norblad.

Kaolin is elutriated, and the finest portions cast into plates in plaster of Paris moulds, burnt at a sintering temperature, broken up and washed on a sieve until uniform particles about 0.5-1.5 mm. in diameter are obtained. The material thus prepared and used in the proportion of 25 grammes to 10 grammes of milk gave results closely approximating to those obtained by the Adams process, and is in every way equal to it save in the greater care needed to transfer it to the extractor.

The conclusions arrived at in this exhaustive and important paper are as follows:—

1. The lactocrite used with a mixture of hydrochloric and lactic acids gives results quite comparable with those obtained by the best gravimetric processes.
2. Kaolin prepared and used as described, and when dry extracted directly with ether, gives figures agreeing with those arrived at by the Adams process.
3. The Adams process leaves nothing to be desired if the strips of paper be first thoroughly extracted with ether.
4. The aerometric method, though giving very small errors for milks containing more than 2.5 per cent. of fat, is unreliable for poor and skim milks, and is altogether of more limited applicability than the foregoing processes.

B. B.

ANALYSIS OF BUTTER AND OTHER FATS. BY J. KÖNIG AND F. HART. (*Zeits f. Anal. Chem.*, Vol. 30, p. 292.)—The authors add one more to the numerous modifications of older methods. Following the proposal of J. West-Knights (*ANALYST*, Vol. 5), they convert the fatty acids into the baryta salts, and estimate the amount of combined baryta. They operate as follows:—About five grammes of the fat are placed in a graduated 300 c.c. flask, 50 c.c. of alcohol are added, heated on the water-bath until all fat is dissolved; 40 c.c. hot baryta solution, containing 17.5 barium hydrate in 100 c.c., are then added, and the mixture boiled under a reflux condenser, with addition of a few pieces of pumice, for three to four hours. The solution is then allowed to cool, water is added to the mark, and filtered. Through 200 c.c. of the filtrate carbonic acid is passed until the reaction is no longer alkaline, the whole is then boiled in a porcelain basin nearly to dryness, allow to cool, make up to 250 c.c., and 200 c.c. filtered off; to the clear filtrate dilute sulphuric acid is added (the original says hydrochloric acid and barium chloride), and the  $\text{BaSO}_4$  weighed. The quantity found is multiplied by 0.657 to obtain the amount of caustic baryta, combined with the soluble fatty acids, this is then multiplied by  $\frac{3}{2}$ . The authors call the figure so obtained the baryta value of the soluble fatty acids. They also make a blank experiment, by the



results of which the original figure is corrected. The following baryta values have been obtained:—

Linseed 18·7, poppy 7·0, olive 9·4, colza 17·6, sesame 6·9, earthenut 22·9, cotton 29·1, liver oils from 25·2 to 52·8, palm-kernel oil 86·3, coco-nut oil 118·5, coco-butter 195·1, six samples of butter-fat 238·5, 216·9, 221·5, 216·4, 236·0, 199·6; beef-fat 35·8, mutton fat 4·9, lard 17·1, three samples of margarine 21·6, 21·7, 22·8.

The baryta value of fats therefore runs, in general, parallel with the Reichert-Wollny figure. In the six samples of butter just quoted the Wollny figure was 30·7, 29·0, 28·7, 28·2, 27·5, 26·3. The variations of the baryta values are, therefore, much wider than those of the volatile fatty acids. It is difficult, therefore, to understand the reasoning by which the authors come to the conclusion that their method surpasses the Reichert-Wollny, as regards simplicity, and equals it as to sharpness of distinction.

O. H.

VOLUMETRIC ESTIMATION OF MANGANESE. BY L. BLUM (*Zeits. f. Anal. Chem.* Vol. 30, p. 284).—This is a modification of Donath and Hattensaur's method (*Chem. Zeit.* 1890, p. 323). It depends upon the fact that in a manganese solution, which contains tartaric acid, ammonium chloride, and a ferric salt, and rendered ammoniacal, potassium ferrocyanide precipitates the whole of the manganese as mangan-ammonium-ferrocyanide. The iron is not precipitated under these conditions. A standard solution is made of 10 grammes cryst.  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in 500 c.c. water; 50 c.c. of this are pipetted into a beaker, a few drops of ferric chloride, 20 c.c. of cold saturated ammonium chloride and 30 c.c. tartaric acid solution and ammonia are added, the fluid heated to boiling, and titrated with a ferrocyanide solution containing 38·487 grammes. pure crystallised potassium ferrocyanide per litre, each c.c. of this being equal to ·005 gramme manganese. The end-reaction is obtained by taking out from time to time a drop of the solution and bringing it together upon a white plate with a drop of dilute acetic acid, which, when the ferrocyanide is in excess, produces the blue colour of prussian blue.

The author compares his method with Volhard's permanganate method, with which it agrees very well. He adds the warning, not to rely implicitly upon the purity of the ferrocyanide, as this salt sometimes contains much sodium in place of potassium.

O. H.

DETECTION OF SESAME OIL IN OLIVE OIL. J. T. TOCHER, A.I.C. (*Pharm. Journ.*, Jan. 24, 1891).—Prepare a solution of pyrogallol in pure hydrochloric acid. Measure  $\frac{1}{2}$  oz. of this solution into a wide-mouthed test tube provided with a cork, and add  $\frac{1}{2}$  oz. (1 oz. if the adulteration be small) of the oil to be tested. Shake well, and allow the oil and acid to separate. Draw off supernatant liquid with pipette, and boil the hydrochloric acid solution for about five minutes, when, if sesame oil be present, the colour of the solution will have changed to purple. The purple develops slowly on boiling. The colour by transmitted light is wine-red to purple, and, by reflected light, blue. Of oils of known composition treated in this way, pure olive gave a faint yellow; sesame, deep purple; 20 per cent. sesame, purple; 5 per cent. sesame, faint purple; 1 per cent. sesame, very faint purple; almond, colourless; ground nut, colourless; cotton-seed, very faint red; sun flower, faint olive; rape, colourless.

# THE ANALYST.

AUGUST, 1891.

## EXPERIMENTS ON THE ESTIMATION OF BORIC ACID.

By OTTO HEHNER.

(Read at Meeting, June 3rd, 1891.)

THE separation of boric acid by means of distillation with methyl alcohol in an acid solution has been recognised by a number of investigators as being capable of securing rapid and accurate results, and certainly furnishes the readiest analytical means for the determination of boric acid in articles of food. The method is at present generally attributed to Gooch ; but it seems to have originated somewhat earlier, or possibly independently, with T. Rosenbladt (*Zeit. f. Anal. Chem.*, Vol. xxvi., p. 18), who distilled a sulphuric acid solution with methyl alcohol, fixed the boric acid contained in the distillate by the addition of a weighed quantity of magnesia, evaporating and igniting. Gooch, recognising that magnesia fixed boric acid only incompletely, or only after some hours of maceration, substituted for it caustic lime, a weighed quantity of which was placed in the receiver, the contents being afterwards transferred to a weighed platinum dish, and the residue obtained by evaporation ignited over the blow-pipe.

Penfield and Sperry (*Amer. Jour. of Sc.* xxxiv., p. 222), recognising the difficulty of igniting to constant weight a comparatively large quantity of caustic lime in a necessarily large platinum dish, modified the method by collecting the distillate, adding it to a weighed quantity of lime contained in a dish, evaporating, scraping out the contents of the dish into a weighed platinum crucible, dissolving adhering particles from the large dish with nitric acid, and adding the solution to the contents of the crucible, which is then ignited to constant weight. This method, clumsy as the transference of a dry residue from one vessel to another must necessarily be, is improved by Cassal (*ANALYST*, Vol. XV., p. 230), who collects the distillate at once into a weighed platinum dish containing the lime ; but this modification of the process does not remove the obvious difficulty of igniting upwards of a gramme of lime to a constant weight in a large platinum basin.

I should here state that the use of lime for fixing boric acid is due to H. Gilbert (*Repert. Anal. Chem.*, Vol: v., p. 375), so that the Gooch method is really a combination of Rosenbladt's distillation method and Gilbert's ignition process.

In order to substitute for the lime other substances capable of fixing boric acid, the investigation was undertaken, of which the results are recorded in this paper. Although some of my results are negative, yet they may be worthy of being brought before you, as clearing up certain points in the chemistry of boric acid about which some difference of opinion existed.

### *Experiments to fix boric acid with ammonia.*

0.4807 gramme of pure boric acid ( $\text{H BO}$ ) were placed in a weighed platinum dish, dissolved in water ; ammonia was added, the solution evaporated, and the residue

obtained first dried at  $100^{\circ}\text{C}$ ., afterwards ignited over an argand to constant weight.

Residue at  $100^{\circ}\text{C}$ .. 0.4138, or 86.08 per cent.

Ignited residue .. 0.2560, or 53.25 per cent.

Theory for  $\text{B}_2\text{O}_3$  56.45 per cent. 0.0898 gramme  $\text{H}_3\text{BO}_3$ , similarly treated with ammonia, yielded 0.0768 gramme at  $100^{\circ}\text{C}$ ., or 85.52 per cent. This residue, repeatedly evaporated with ammonia, diminished steadily in weight to 0.0620, 0.0432, 0.0340, and 0.0263 gramme, or 34.2 per cent., at which point the evaporation was not continued, it being demonstrated that boric acid is volatile in presence of ammonia.

This agrees with the observation of Bodewig (*Zeit. fur. Anal. Chem.*, Vol. xxiii., p. 149), who states that upon evaporation of a solution of ammonium borate on the water-bath a point is reached at which the vapours were alkaline, but the liquor acid.

*Experiments to fix with sodium carbonate.*

It is well known that boric acid can be completely fixed by sodium carbonate; but the statements as to the amount of carbonic acid driven out by the boric acid are very contradictory. According to Bloxam, one molecule of boric acid displaces on gentle ignition one molecule of carbonic acid, but at a strong red heat from 1.5 to 2.3 molecules; whilst according to Schaffgotsh one equivalent of  $\text{H BO}_3$  expels all carbonic acid from two molecules of sodium carbonate.

I could not obtain, in the few experiments I made in this direction, any results of sufficient accuracy for analytical purposes. To 0.5598 gramme pure boric acid ( $\text{H}_3\text{BO}_3$ ), 2.7824 grammes dry pure  $\text{Na}_2\text{CO}_3$  were added, and the mixture heated to constant weight. The loss, including 43.55 per cent. of water yielded by the boric acid amounted to 102.03 per cent. of the boric acid taken, corresponding to 58.48 per cent. of  $\text{CO}_2$ , or for one equivalent of  $\text{H}_3\text{BO}_3$ , 0.824 of an equivalent of  $\text{CO}_2$ .

In a second experiment the loss amounted to 104.89 per cent., or 61.34 per cent.  $\text{CO}_2$ , equal to 0.864 equivalents of  $\text{CO}_2$ .

As Bloxam's statements are doubtless for the old equivalents, his figures become comparable by halving them, when they are 0.75 to 1.15.

It is almost impossible to obtain constant weights, and I, therefore, abandoned the attempt.

*Experiments to fix with sodium phosphate.*

A solution of sodium phosphate was made, containing about 20 grammes pure crystallised sodium phosphate per litre.

25 c.c. of this were evaporated, the residue first very gently heated over the smallest possible argand flame (to avoid loss by spurting), and then gradually over a large argand flame, the residue never being permitted to become red-hot. The residue weighed 0.1856 gramme. According to the fifth edition of "Fresenius' Quantitative Analysis," at this temperature all water of crystallisation is driven off; but not constitutional water. This statement, however, is not correct, because on strong ignition of the above residue over a Bunsen flame, the weight remained perfectly constant. In the newest edition of Fresenius, I must add, this erroneous statement is omitted.

0.0632 gramme pure boric acid ( $\text{H}_3\text{BO}_3$ ) was evaporated with 10 c.c. of the phosphate solution, yielding 0.0742  $\text{Na}_2\text{P}_2\text{O}_7$ . The residue consisted of a perfectly transparent gummy mass, and was ignited most cautiously, as it is very apt to spurt, over a small

argand flame in a covered platinum basin, the heat being ultimately increased until the residue had fused. It weighed 0.1082 gramme, containing, therefore, 0.034 gramme  $B_2O_3$ , against 0.0356  $B_2O_3$  taken, loss 0.0016.

0.0691 gramme  $H_3BO_3$ , corresponding to 0.0390 gramme  $B_2O_3$ , plus 20 c.c. phosphate solution (0.1483 pyrophosphate), yielded 0.1863 gramme ignited residue, or 0.0380  $B_2O_3$ —loss 0.0010.

This residue was evaporated with repeated quantities of water, in all 200 c.c.; the dry mass was again ignited; loss of weight, none.

0.1100 gramme  $H_3BO_3$ , equal to 0.0621 gramme  $B_2O_3$ , was evaporated with 50 c.c. sodium phosphate solution (0.3712 pyrophosphate), yielded 0.1340 gramme residue, or 0.0628 gramme  $B_2O_3$ +0.0007.

0.1008 gramme  $H_3BO_3$ , equal to 0.0569  $B_2O_3$ , evaporated with 35 c.c. sodium phosphate solution, containing 0.2598 gramme pyrophosphate, and then with 250 c.c. of distilled water in several portions. Ignited residue 0.3166, equal to 0.0568  $B_2O_3$ ; loss 0.0001.

To ascertain the minimum quantity of phosphate necessary to fix the boric acid a few experiments were made, which indicated, as far as they went, that one molecule of  $Na_2HPO_4$  is capable of binding 2 molecules of  $H_3BO_3$ , the resulting mass consisting of sodium metaphosphate and borax.

To 0.1785 gramme  $H_3BO_3$  a quantity of sodium phosphate was added, capable of yielding 0.1916 gramme of pyrophosphate, this being the above molecular proportion. Residue obtained, 0.2894 gramme, or 0.0978  $B_2O_3$ ; loss, 0.0029.

0.1792 gramme  $H_3BO_3$  (0.1015  $B_2O_3$ ) evaporated with 25 c.c. of water, without the addition of phosphate, and the residue ignited, yielded 0.0889 gramme  $B_2O_3$ , a loss of 0.0122 gramme, plainly showing the fixing influence of the sodium phosphate.

To ascertain whether this was in any way affected by the presence of alcohol, 0.1606 gramme  $H_3BO_3$  (0.0906  $B_2O_3$ ) were dissolved in 100 c.c. methylated spirit, 150 c.c. water added, and a quantity of phosphate solution, yielding 0.3832 gramme pyrophosphate; the mixture was then boiled in a covered beaker until all alcohol had evaporated; the remainder was transferred to a weighed platinum basin, evaporated, and the residue ignited. Obtained 0.4710, or 0.0878  $B_2O_3$ , a loss of 0.0028.

The advantage of adding a soluble salt, which easily parts with its water, and which combines by direct addition with the boric acid to be estimated over a substance like lime, which incrustates the vessels and attracts carbonic acid, which is difficult to remove, is obvious. I am not sure that sodium phosphate is the best possible salt that could be chosen; but the results yielded by its use are fairly satisfactory, and certainly very rapidly obtained. I only ascertained after the above analyses were completed that Stolba had long ago proposed to fix boric acid in solution by adding a weighed quantity of borax (about four times the weight), and igniting the residue (*Jour. f. Prar. Chem.*, xc., p. 479). I have made experiments in this direction and find that very good results may be obtained, but that the greatest caution is necessary to avoid loss by crepitation during the ignition of the residue.

Incidentally I may observe that boric acid cannot be alkalimetrically determined, as no indicator is at present known which allows of anything like a sharp titration;

and this in spite of the curious fact that Guyard (*Bullet. Soc. Chem.*, xl., p. 422) has recommended pure crystallised boric acid as an alkalimetric standard; logwood, which he recommends as an indicator, fails utterly to yield a sharp colour change with the acid.

I further wish to correct the statement found in books, that boric acid, when heated in a water-oven at 100°C. loses two-thirds of its water. Boric acid placed in a water-oven loses weight steadily, until the whole of it is volatilised, and no definite point at any stage can be observed.

Thus 0.0736 gramme  $H_2BO_3$  kept for three or four days at 100° C. diminished to 0.0179 gramme, or 24.3 per cent. of the original weight. This small residue ignited yielded 0.0108  $B_2O_3$ , or 60.34 per cent. of its weight. If the residue had consisted of  $H_2B_2O_4$ , as stated in the books, 72.7 per cent. ought to have remained. Of course, the determination cannot be very exact, seeing that it was made with a few milligrammes only; but the experiment proves sufficiently that by mere drying in the water bath no definite stage of composition can be reached.

Lastly, I record the observation, that if *anhydrous* boric acid is dissolved in cold water, the turmeric reaction is not obtained, or, at least, only exceedingly faintly, in comparison with an equivalent proportion of hydrated acid, whilst a strong reaction is at once obtained if a trace of mineral acid is added. This furnishes proof that boric anhydride dissolves as such, and does not immediately hydrate on being dissolved in water. The pieces of turmeric paper dried with solution of anhydrous boric acid gradually turn red when allowed to lie in the air of the laboratory.

This observation suggests some interesting speculations, with the testing of which I am at present engaged—namely, does there exist a series of pyroborates, just as there are pyrophosphates and pyrosulphates, and can their existence be analytically proved? In the case of the phosphates, the colour of the silver salts at once shows the difference, whilst in that of the pyrosulphates, two reactions are due to E. Drechsel (*Jour. f. Pract. Chemie*, v., p. 367), distinguishing pyro from acid sulphates. Anhydrous borax is, of course, pyroborate of sodium,  $Na_2B_4O_7$ ; but all the reactions of borates are those of the ortho acid  $H_3BO_3$ , and ordinary borax is certainly the acid ortho salt. The difficulty experienced in rendering boric acid anhydrous renders it most unlikely that by simple addition of soda in an aqueous solution, a molecule of anhydrous acid is produced, which combines with the neutral salt  $Na_2B_2O_4$ . Borax according to this view would be  $Na_2H_2B_4O_8 + 9 H_2O$ , and boric acid  $H_4B_4O_8 + H_2O$ . The evidence that boric acid is tribasic is exceedingly slight.

#### DISCUSSION.

MR. BLOUNT said that Mr. Hehner's method was extremely ingenious; but the objection to the lime process was not insuperable. He himself was in the habit of igniting lime to perfect causticity by the simple plan of using a muffle. It was the use of the blow-pipe, which he regarded as extremely unsuitable for this purpose, which caused all the trouble.

MR. CASSAL said that the substitution of phosphate of soda for lime, in the method suggested by Mr. Hehner, was certainly a valuable improvement, since under the most favourable circumstances, to get the lime to constant weight was very troublesome. He desired to take the opportunity of stating that in abstracts which had appeared of a

paper read some time ago by himself, the introduction of methyl alcohol to separate boric acid had been erroneously attributed to him. He could confirm what Mr. Hehner had said about the turmeric test; it was necessary to add hydrochloric acid when dealing with anhydrous boric acid.

## THE EFFECT ON BUTTER FROM FEEDING ON COTTON-SEED AND COTTON-SEED MEAL.

By N. T. LUPTON.

(*Journal of the American Chem. Society*, Vol. xiii., April, 1891.)

AN investigation was undertaken a few months ago at the Alabama Experiment Station to determine the effect of cotton-seed and cotton-seed meal on the composition of butter-fat, especially on the volatile acids, the melting point, and the specific gravity of the butter produced.

Several chemists of late years have called attention to changes produced by the use of the feed-stuffs mentioned, notably Prof. Harrington, of the Texas Experiment Station, and Dr. Wiley, of the Department of Agriculture, Washington, D.C. This subject was thought to be of sufficient scientific and practical importance to justify an extended investigation. For this purpose, a herd of registered Jerseys was divided into two groups, one consisting of ten cattle and the other of a single cow. The cattle of the first group were fed for a preparatory period of ten days on the customary ration used at the station, excluding cotton-seed meal and hulls, the single cow was fed on the same ration. At the end of the preparatory period, samples of milk and butter were taken for one week, on Monday, Wednesday, and Friday, and carefully analysed. The milk of the ten cattle composing the first group was mixed and churned as a whole. That of the single cow was kept separate and churned by itself. The first preparatory period was for ten days; after that, the experimental and preparatory periods extended over seven days each.

The daily rations for the different periods which represent the kind and quantity of food actually consumed, were as follows:—

### 1st period, preparatory and experimental.

|                   |    |    |    |       |        |
|-------------------|----|----|----|-------|--------|
| Ground oats       | .. | .. | .. | ..    | 5 lbs. |
| Ground corn       | .. | .. | .. | ..    | 5 „    |
| Bran              | .. | .. | .. | ..    | 5 „    |
| Nutritive ratio.. | .. | .. | .. | 1:5.8 |        |

### 2nd period.

|                   |    |    |    |        |        |
|-------------------|----|----|----|--------|--------|
| Cotton-seed meal  | .. | .. | .. | ..     | 3 lbs. |
| Ground oats       | .. | .. | .. | ..     | 4 „    |
| Bran              | .. | .. | .. | ..     | 5 „    |
| Ensilage          | .. | .. | .. | ..     | 11 „   |
| Nutritive ratio.. | .. | .. | .. | 1:3.75 |        |

## 3rd period.

|                     |    |    |    |        |        |
|---------------------|----|----|----|--------|--------|
| Cotton-seed meal .. | .. | .. | .. | ..     | 4 lbs. |
| Cotton-seed hulls.. | .. | .. | .. | ..     | 9 "    |
| Ensilage ..         | .. | .. | .. | ..     | 4½ "   |
| Nutritive ratio ..  | .. | .. | .. | 1:5.08 |        |

During the fourth period the cattle were confined exclusively to raw cotton-seed and cotton-seed hulls ; and during the fifth period to cooked cotton-seed and cotton-seed hulls ; they were allowed as much as they would eat. The nutritive ratios mentioned above are calculated from analyses made of the feed-stuffs in use at the station. In compounding the rations, the object was not so much to conform with strictness to the German standard as to bring the cows gradually under the influence of cotton-seed, cotton-seed meal and hulls, without injury to their general health.

The results of the analysis of samples of milk and butter, taken immediately after each milking and churning, are given below. The first two tables give the composition of each sample of milk analysed, also the volatile acids, melting point and specific gravity of the butter from the same milk ; the third table gives the average composition for each experimental period.

Composition of Jersey Milk for each day analysed.

Butter from same Milk.

| Date.    | Water.    | Butter Fat | Casein.   | Sugar.    | Ash.      | Volatile Acids.                                | Melting point. | Sp. gr. at 100° C. | Rations. |
|----------|-----------|------------|-----------|-----------|-----------|--|----------------|--------------------|----------|
| Group I. | per cent. | per cent.  | per cent. | per cent. | per cent. | c.c. $\frac{1}{10}$ normal alkali for 5 grams. | °C             |                    | Period.  |
| Nov. 19  | 85.76     | 5.53       | 3.95      | 3.96      | .80       | 30.0   | 35.9           | .9026              | 1        |
| " 21     | 84.95     | 5.20       | 4.05      | 5.09      | .81       | 29.6   | 35.3           | .9031              |          |
| Dec. 1   | 84.15     | 5.73       | 4.06      | 5.24      | .82       | 29.7   | 36.0           | .9041              | 2        |
| " 3      | 83.62     | 5.51       | 3.88      | 6.19      | .80       | 30.5   | 36.3           | .9016              |          |
| " 5      | 84.26     | 5.16       | 3.90      | 5.98      | .80       | 31.4   | 36.1           | .9026              |          |
| " 15     | 84.53     | 5.96       | 3.64      | 5.12      | .75       | 28.4   | 36.6           | .9008              | 3        |
| " 17     | 83.35     | 6.07       | 3.60      | 6.03      | .75       | 26.9   | 37.6           | .9019              |          |
| " 19     | 84.71     | 5.79       | 3.57      | 5.19      | .74       | 27.1   | 38.1           | .9031              |          |
| Jan. 5   | 84.27     | 6.41       | 3.58      | 5.01      | .73       | 22.0   | 43.6           | .9002              | 4        |
| " 7      | 84.59     | 6.11       | 3.34      | 5.22      | .74       | 21.9   | 43.9           | .8972              |          |
| " 9      | 84.51     | 5.84       | 3.56      | 5.37      | .72       | 22.4   | 43.4           | .8995              |          |
| " 19     | 85.84     | 4.87       | 3.39      | 5.16      | .74       | 23.1   | 42.7           | .9046              | 5        |
| " 21     | 84.89     | 5.95       | 3.31      | 5.08      | .77       | 22.2   | 42.3           | .9006              |          |
| " 23     | 85.38     | 5.53       | 3.31      | 5.04      | .74       | 22.1   | 43.0           | .9027              |          |

| Composition of Jersey Milk for each day analysed. |           |            |           |           |           | Butter from same Milk.                         |                |                    |          |
|---|-----------|------------|-----------|-----------|-----------|--|----------------|--------------------|----------|
| Date.   | Water.    | Butter Fat | Casein.   | Sugar.    | Ash.      | Volatile Acids.                                | Melting point. | Sp. gr. at 100° C. | Rations. |
| Group II.   | per cent. | per cent.  | per cent. | per cent. | per cent. | c.c. $\frac{1}{16}$ normal alkali for 5 grams. | °C             |                    | Period.  |
| Nov. 24   | 85.53     | 4.67       | 3.84      | 5.23      | .73       | 31.4   | 35.1           | .9019              | 1        |
| " 28  | 84.03     | 5.93       | 3.93      | 5.30      | .81       | 31.5   | 33.4           | .9046              |          |
| Dec. 8  | 85.71     | 4.75       | 3.56      | 5.30      | .68       |  |                |                    | 2        |
| " 10  | 85.68     | 4.53       | 3.84      | 5.24      | .71       | 31.7   | 36.5           | .9028              |          |
| " 12  | 85.63     | 3.94       | 3.66      | 6.02      | .75       | 30.6   | 36.2           | .9002              |          |
| " 22  | 85.26     | 4.74       | 3.42      | 5.86      | .72       | 25.5   | 37.5           | .9019              | 3        |
| Jan. 2  | 84.31     | 5.85       | 3.69      | 5.42      | .73       | 25.4   | 41.3           | .8980              |          |
| " 12  | 85.17     | 5.12       | 3.40      | 5.60      | .71       | 20.5   | 43.5           | .8975              | 4        |
| " 14  | 85.10     | 4.76       | 3.47      | 5.98      | .69       | 19.2   | 41.0           | .8993              |          |
| " 16  | 85.54     | 4.80       | 3.34      | 5.64      | .68       | 21.4   | 43.0           | .8988              |          |
| " 26  | 86.21     | 4.87       | 3.13      | 5.09      | .70       | 22.0   | 43.3           | .8977              | 5        |
| " 28  | 86.00     | 4.88       | 3.12      | 5.28      | .72       | 22.1   | 43.3           | .8999              |          |
| " 30  | 85.39     | 6.00       | 3.18      | 4.72      | .71       | 21.7   | 44.0           | .8980              |          |

Average Composition of Jersey Milk during each Period.

Butter from same Milk.

| Period.   | Water. | Butter Fat. | Casein. | Sugar. | Ash. | Volatile Acids. | Melting Point. | Sp. Gr. at 100°C. | Rations. |
|-----------|--------|-------------|---------|--------|------|-----------------|----------------|-------------------|----------|
| Group I.  |        |             |         |        |      |                 |                |                   |          |
| I.        | 85.35  | 5.36        | 4.00    | 4.52   | .81  | 29.8            | 35.6           | .9028             | 1        |
| II.       | 84.01  | 5.47        | 3.95    | 5.80   | .81  | 30.5            | 36.1           | .9028             | 2        |
| III.      | 84.20  | 5.91        | 3.60    | 5.45   | .75  | 27.5            | 37.4           | .9019             | 3        |
| IV.       | 84.46  | 6.12        | 3.49    | 5.20   | .73  | 22.1            | 43.6           | .8990             | 4        |
| V.        | 85.37  | 5.45        | 3.36    | 5.09   | .75  | 22.5            | 42.7           | .9026             | 5        |
| Group II. |        |             |         |        |      |                 |                |                   |          |
| I.        | 84.78  | 5.30        | 3.89    | 5.26   | .77  | 31.4            | 34.2           | .9032             | 1        |
| II.       | 85.67  | 4.41        | 3.69    | 5.52   | .71  | 31.1            | 36.3           | .9015             | 2        |
| III.      | 84.79  | 5.30        | 3.37    | 5.64   | .72  | 25.45           | 39.4           | .8999             | 3        |
| IV.       | 85.27  | 4.89        | 3.40    | 5.74   | .69  | 20.4            | 42.5           | .8986             | 4        |
| V.        | 85.87  | 4.92        | 3.14    | 5.03   | .71  | 21.9            | 43.5           | .8986             | 5        |

The following table, taken from a record carefully kept at the dairy, gives the



aggregate amount of milk and butter produced by the first group, consisting of ten cows, for each experimental period of seven days :—

| Period |    | Pounds of Milk. |    | Pounds of Butter. |    | Pounds of Milk<br>for 1 lb. of Butter. |
|--------|----|-----------------|----|-------------------|----|--|
| 1      | .. | 1414½           | .. | 82                | .. | 17·2                                   |
| 2      | .. | 1275            | .. | 85½               | .. | 14·9                                   |
| 3      | .. | 975             | .. | 91                | .. | 10·7                                   |
| 4      | .. | 896             | .. | 75                | .. | 11·9                                   |
| 5      | .. | 716             | .. | 58                | .. | 12·3                                   |

As will be observed, there is a marked falling off in the quantity of milk and a corresponding increase in the amount of butter produced during the first three periods, as the cattle were getting more under the influence of cotton-seed meal.

During the remaining periods, the quantities of both butter and milk diminish, the ration being confined to cotton-seed and cotton-seed meal, without reference to having it well balanced as a milk ration.

The general effects of these valuable feed-stuffs, when used in carefully prepared rations, will hereafter be investigated. At present we are concerned only, as previously stated, with their effects on the volatile acids, melting point and specific gravity of the butter-fat produced under their influence. For these effects attention is called to the above tabular statements, from which the following conclusions are drawn :—Feeding on cotton-seed and cotton-seed meal increases, in a marked degree, the melting point of butter, the increase reaching in these experiments eight or nine degrees, and diminishes to a corresponding extent the volatile acids, while the specific gravity remains virtually the same.

The richness of cotton-seed meal in albuminoids renders it of prime importance to mix it with one or more food stuffs poor in this nitrogenous compound, such as ensilage, hay, or cotton-seed hulls.

It may be stated in this connection, that no change was observable in the colour of the butter from feeding with cotton-seed and cotton-seed meal. The samples, still in the laboratory, are all of a beautiful golden yellow.

It is proper to state that the analytical work in the above tables was done by Dr. J. T. Anderson, first assistant in the chemical laboratory.

## THE ANALYSIS OF BEESWAX.

C. MANGOLD.

(*Chem. Zeit.* 1891, 15, 799, 800.)

ON account of the natural fluctuations of the so-called constants of yellow beeswax, such as the acid and saponification numbers, as well as the iodine number determined by the Hübl process, adulteration with less than 6 per cent. of paraffin or ceresin is difficult to detect.

A. and P. Buisine, applying (*Bull. Soc. Chem.* 1890, 3, 567) the principle previously enunciated by Hell, Stürcke and Schwalb, have devised a method of sufficient apparent value to warrant its investigation at the hands of the author.

The wax is saponified with potash and heated with potash lime, by which treatment the higher alcohols are converted into fatty acids with elimination of hydrogen, which serves as a measure of their amount. The hydrocarbons present are unattacked and can be extracted from the residue.

The author's investigations confirm those of A. and P. Buisine, and have led him to

recommend the following method :—2—10 grammes of the wax are melted and saponified by potash-lime, the reaction being aided by stirring. The saponified product is powdered when cold, intimately mixed with three times its weight of potash-lime, and the mixture transferred to a thick-walled, pear-shaped bulb-tube, which is heated to 250° C. (for two hours according to Buisine, *c.f.*, the time adopted by the author below) in a mercury-bath contained in an iron vessel. This vessel is provided with a lid which screws on air-tight, pierced with four apertures through which pass air-tight, respectively, the pear-shaped bulb, a thermometer, a thermostat, and a long tube open at both ends to condense any mercury which may volatilise. A tube connects the pear-shaped bulb with a Hofmann's burette, in which the hydrogen is measured.

Although the author has made some determinations of its amount (obtaining results somewhat lower than those of Buisine), his attention has been chiefly directed to the estimation of the hydrocarbons present. Having observed, however, that the volume of hydrogen only becomes constant when the heating has been continued for three hours, he adopts this time as the minimum necessary for the determination of the hydrocarbons. After the completion of the reaction, the residue in the bulb-tube and the bulb-tube itself are powdered and extracted for some hours with petroleum ether in a Soxhlet's tube, the ether distilled off, and the residual hydrocarbon dried at 110° C. and weighed.

Schwab has already noted (*Annalen*, 1886, 235, 149) that pure beeswax itself contains about 6 per cent. of hydrocarbons; while A. and P. Buisine have found as much as 12·5—14 per cent., a result confirmed by the author. In endorsing this statement, he arrived at the conclusion that as little as 2 per cent. of foreign hydrocarbons may be detected. The best approximation to the true proportion of paraffin is said to be obtained by assuming the quantity of hydrocarbons normally present in beeswax to be 13·5 per cent.

The following table gives some figures for unbleached beeswax of diverse origins :—

| Source of sample.       | Hydrocarbons. | Acid number. | True saponification number (after deduction of acid number.) |
|-------------------------|---------------|--------------|--|
| Aussee .. .. .          | 13·51         | 19·79        | 72·51  |
| Native .. .. .          | 13·75         | 20·44        | 70·65  |
| " .. .. .               | 14·72         | 20·12        | 67·84  |
| Dalmatia .. .. .        | 14·51         | 18·81        | 71·99  |
| Hungary .. .. .         | 14·60         | 23·04        | 66·55  |
| Bosnia (Banjaluka) ..   | 14·27         | 19·31        |  |
| Slavonia .. .. .        | 13·76         | 20·95        | 70·23  |
| Carniola .. .. .        | 13·64         | 20·08        | 69·62  |
| Bosnia (Dolna-Tulza) .. | 13·32         | 20·02        | 70·37  |
| Lower Styria .. .. .    | 14·34         | 18·26        | 72·50  |
| Lower Austria .. .. .   | 13·72         | 20·58        | 67·83  |
| Mozambique .. .. .      | 13·37         | 19·42        | 71·78  |
| Chili .. .. .           | 13·35         | 19·99        | 70·01  |
| Monte Cristo .. .. .    | 13·50         | 20·24        | 67·45  |
| Morocco .. .. .         | 11·02         | 21·66        | 77·02  |
| Bombay .. .. .          | 14·04         | —            | —  |
| Madagascar .. .. .      | 11·77         | 20·03        | 72·85  |
| Saffi .. .. .           | 12·20         | 19·92        | 73·48  |
| Oran .. .. .            | 11·55         | 19·91        | 79·99  |
| Massanah .. .. .        | 12·80         | 21·11        | 69·49  |
| Mogador .. .. .         | 11·40         | 20·85        | 75·55  |

A sample of yellow beeswax from Transylvania had an acid number of 16.66, and a total acid number of 72.68; that is to say, a true saponification number of 56.02, plainly indicating that it was adulterated with paraffin or some similar hydrocarbon. The total percentage of hydro-carbons was 28.12, corresponding to an addition of 17 per cent. of paraffin calculated on the original wax. The percentage of hydrocarbons and the total acid number of the mixture being known, the total acid number of the original wax could be calculated, and was found in this case to be 87.6. A mixture made by adding 8 per cent. of paraffin to a genuine sample of beeswax gave figures on analysis corresponding to an addition of 7.4 per cent.

A few figures for bleached beeswax are also given.

| Source of sample.  | Hydrocarbons. | Acid number. | True saponification number (after deduction of acid number). |
|--------------------|---------------|--------------|--|
| Smyrna .. ..       | 10.93         | 20.87        | 68.33  |
| Egypt .. ..        | 11.35         | 20.04        | 69.94  |
| Transylvania .. .. | 13.61         | 24.68        | —  |
| Hungary .. ..      | 15.48         | 23.05        | *79.49   |

According to A. and P. Buisine, bleached wax gives a lower result for hydrocarbons than yellow wax; the last two samples are apparently impure, and have been bleached by chemical means.

B. B.

## A NEW TEST FOR ALBUMEN AND OTHER PROTEIDS.

By J. A. MACWILLIAM.

(From *Chem. and Drug.* after *B. Med. Journ.*)

THE test employed is salicyl-sulphonic acid ( $C_6H_3.OH.SO_3H.CO_2OH$ ), which is made by the action of sulphuric anhydride on salicylic acid, or by heating salicylic acid with concentrated sulphuric acid. The product is an exceedingly delicate and precise test for the detection of all proteids in solution, the presence of which it reveals by the formation of a dense white precipitate, which becomes flocculent on heating. Various substances classed under native albumens, derived albumens, globulins, fibrin, albumoses, and peptones have all been tried, and all respond to the test; but the precipitates of albumoses and peptones are redissolved on heating, which distinguishes them from albumens and the like. The test is applied by adding a few drops of a solution of the acid to the solution of the proteid. The precipitate forms at once, or, in the case of very dilute solutions, within one minute a cloudiness appears. To give some idea of the delicacy of the test Professor MacWilliam provides data of experiments. From these we note that a solution of egg albumen, 1 in 2,000, gave no reaction on boiling in presence of excess of acetic acid. A 1 in 8,000 solution also failed to respond to the xantho-proteid, Heller's, and the mercurio-potassic iodide tests, although it gave a distinct opalescence with the salicyl-sulphonic acid test—indeed, the same was obtained with a 1 in 12,500 solution. It

\* 74.49 in original.

was applied to other proteids with equally satisfactory results. The test is, of course, intended for the detection of albumen in urine. In view of the number of substances which may occur in that fluid which might react with the test, Professor MacWilliam gives results of careful experiments, which show that (1) the precipitate is a proteid one; (2) it is always obtained when proteid is present in the various abnormal conditions of urine; (3) it is not given by non-proteid substances, such as phosphates, urates, mucin, the alkaloids, and drugs generally; (4) for delicacy and precision it surpasses all other tests; the only one approaching it is the mercurio-potassic iodide test, and this gives copious precipitates with alkaloids and other substances.

It is evident that the test is one of great delicacy for the detection of albumen in urine, and, as it is more easily performed than even the simple boiling test, it will doubtless rapidly become popular. The manner of applying the test is as follows:—

Take a small amount of urine (for example, 20 minims), preferably in a very small test-tube, and add a drop or two of a *saturated* watery solution of the reagent. If the urine is strongly alkaline, an extra drop or two of the acid should be added, and if no opalescence or precipitate occurs it is well to test the reaction with litmus-paper, and make sure that the urine has been rendered strongly acid. On adding the reagent, shake the tube quickly so as to mix its contents. Then examine at once. The occurrence of an opalescence or cloudiness *immediately or within a very few seconds* (for example, two or three seconds) is a test for proteids intermediate in delicacy between the cold nitric acid test on the one hand and the acetic acid and heat test (in favourable circumstances) on the other. The development of an opalescence some time after (one-half to two minutes) is a more delicate test than even acetic acid and heat, and shows the presence of minute traces of proteid, which are probably insignificant, from a clinical point of view, as a rule.

Next heat the tube to the boiling point. If the precipitate or opalescence is caused by the ordinary "albumen" (albumen and globulin) commonly present in albuminous urine, it does not disappear on heating, but, on the other hand, becomes markedly flocculent. But if the precipitate or opalescence is due to the presence of albumoses or peptones, it clears up on heating (before the boiling point is reached) and reappears when the tube cools.

Salicyl-sulphonic acid, or sulpho-salicylic acid, occurs in colourless, long, thin, needle-shaped crystals, which are very soluble in water, and melt at 120° C. It must not be confounded with salicyl-sulphuric acid ( $C_6H_4.SO_4H.CO_2H$ ). Salicyl-sulphonic acid is best made by heating salicylic and sulphuric acids together, allowing the new-formed acid to crystallise out, collecting and recrystallising from warm water. The acid gives an intense reddish-violet colour with ferric chloride.

## ANALYSIS OF GREY COPPER ORE, ETC.

By W. HAMPE.

(*Chemiker Zeitung*, No. 26, 1891.)

For dissolving minerals or metallurgical products which contain arsenic, antimony and perhaps tin, the best plan is to use a mixture of nitric and tartaric acids. This

has the advantage over nitro-hydrochloric acid, or hydrochloric acid and chlorate of potash, or bromine water, as there is no need for any precautions to prevent volatilisation of arsenic. It has the advantage over nitric acid alone, that there remains no residue of antimonious or stannic acid contaminated with lead or copper, which, of course, greatly simplifies the analysis.

The tartaric acid must first be tested as to its purity. The watery solution must not be precipitated by hydrogen sulphide (absence of lead, tin) or rendered turbid by ammonia and ammonium sulphide. For one gram. of the mineral, grey copper ore, for instance, I use 10 grams of tartaric acid and about 30 c.c. of nitric acid, and allow the mixture to stand for some hours in a warm place. If the sample contains no, or but little, sulphur, it dissolves clear, but there generally remains a little undissolved sulphur. This must be filtered off and treated with warm solution of potassium sulphide. The obtained is kept and afterwards united with the main solution of the sulphides of arsenic, antimony and tin. If the potassium sulphide should leave a residue consisting of undecomposed mineral, this should be again treated with the acid mixture and the solution obtained added to the first filtrate. This liquid is now heated up to 60° C, and saturated with hydrogen sulphide. After standing for twelve hours, it is again treated with the gas until it is certain that every trace of arsenic is deposited. The precipitate is then filtered off and extracted in the usual manner with potassium sulphide, the resulting solution of arsenic, antimony and tin filtered off, and those metals reprecipitated by dilute sulphuric acid. After filtration their sulphides are dissolved off the filter by means of freshly-prepared ammonium sulphide, and this solution evaporated nearly to dryness. Hydrochloric acid and potassium chlorate are now added, and when all is oxidised, some tartaric acid. After addition of ammonia, the arsenic is thrown down with magnesia mixture. The presence of tin does not interfere.

The magnesium ammonium arseniate is freed from any tartrate by redissolving in hydrochloric acid and reprecipitation with ammonia. If the amount is small, I dissolve it in nitric acid, evaporate the solution and finally gently ignite the residue to convert it into magnesium pyro-arseniate; but if large, I operate as follows:—

The precipitate is again dissolved in hydrochloric acid, the liquid freed from arsenic by means of hydrogen sulphide, and after concentration, precipitated by ammonia and sodium phosphate. The magnesia is finally converted in the usual way into pyro-phosphate. The united filtrates of the ammonium magnesium arseniate are acidified and treated with hydrogen sulphide to throw down the tin and antimony, which are finally separated by Rose's process.

As regards the treatment of the precipitate which is insoluble in the potassium sulphide, I have nothing important to add. The filtrate from the hydrogen sulphide precipitate must, as it contains tartaric acid, be precipitated by ammonia and ammonium sulphide to throw down iron, cobalt, nickel and zinc. These are then separated by the usual methods.

To estimate the sulphur, 1 gram of the sample is fused in a platinum crucible with 6 grams. of nitre and 5 grams of dry soda, the mixture being covered with a layer of nitre. The mass is extracted with water, and any lead removed by a current of carbonic acid. After evaporation with excess of hydrochloric acid, the sulphur is precipitated as usual with barium chloride.

**A Modification of the Reichert Distillation Process.** H. Leffmann and W. Beam (a pamphlet\*).—In order to obviate entirely the use of alcohol in the saponification of butter and other fats, the authors adopt the following mode of procedure:—The saponification is effected by a mixture prepared by adding 25 c.c. of a clear 50 per cent. solution of sodium hydroxide to 125 c.c. of pure glycerine, and boiling for fifteen to twenty minutes to evaporate the greater portion of the water.

About 5 grammes of the clear fat are weighed out in a flask in the usual manner, 10 c.c. of the alkali-glycerine added, and the flask heated over a Bunsen burner. The mixture may foam somewhat; this may be controlled, and the operation hastened by shaking the flask. When all the water has been driven off, the liquid will cease to boil, and if the heat and agitation be continued for a few moments complete saponification will be effected, the mixture becoming perfectly clear. The whole operation will require less than five minutes. The soap is then dissolved in 90 c.c. of water. The first portions of water should be added drop by drop, and the flask shaken between each addition in order to avoid foaming. When the soap is dissolved, 50 c.c. of diluted sulphuric acid (25 c.c. of the concentrated acid to the litre) are added, a piece of pumice dropped in, and the distillation conducted as usual. Blank experiments have given the authors a distillate requiring from 0.2 to 0.3 c.c. decinormal alkali.

The alkali-glycerine is quite viscid when cold. It should be kept in a flask closed with a rubber stopper, and heated when the measured portion is to be taken. O. H.

**On the Digestibility of the Albuminoids of Cocoa.** A. Stutzer. (*Zeitschr. f. Angew. Chem.* 1891, p. 368.)—The value of cocoa as a food is not unfrequently over-estimated. Its nitrogenous substances consist of ammonia, theobromine, amides, and albumen, part of which is digestible, part quite indigestible. The non-proteids are soluble in neutral, aqueous solution in presence of cupric hydrate, the proteids being insoluble under these conditions. In 1 gramme the total nitrogen is estimated by Kjeldahl. For non-proteids 2 grammes are mixed with cupric hydrate and washed with cold water, and from the filtrate the ammonia is liberated by magnesia and distilled off. Cocoa-powder, partly deprived of its fat, contains only traces, certainly less than 0.1 per cent. of nitrogen as ammonia, unless ammonia has been employed for the purpose of rendering the cocoa soluble. The theobromine is determined by boiling out 20 grammes of the sample, precipitating the albuminoids from the solution with ferric acetate, and in the filtrate the theobromine by phospho-tungstic acid, the nitrogen being estimated in the precipitate. The difference in soluble nitrogen is calculated into amides. Theobromine nitrogen multiplied by 3.15...theobromine, amide nitrogen by 6.25...amides. The indigestible albumen is determined by digesting a weighed quantity of the powder first with an acid pepsine solution, then with an alkaline one of pancreas. The matter remaining insoluble is filtered off and Kjeldahled. To obtain exact determinations it is advisable previously to remove all the fat from the sample by ether. The author found in four samples the following amounts of albuminoid nitrogen:

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\* 715, Walnut Street, Philadelphia.

|   |      |      |      |      |
|---|------|------|------|------|
| Nitrogen in soluble albumen . .                                 | 1.64 | 1.23 | 1.68 | 1.2  |
| Nitrogen in insoluble albumen                                   | 1.15 | 1.47 | 1.23 | 1.28 |
| For every 100 parts of digestible albumen the samples contained |      |      |      |      |
| indigestible nitrogen . .                                       | 70   | 119  | 73   | 102  |

That much of the nitrogen becomes indigestible by the roasting which cocoa undergoes during the process of manufacture is shown by the following figures obtained from the unroasted cocoa beans. While of the total nitrogen of the samples of cocoa powder just referred to 31.2, 44.5, 31.2, and 35.8 per cent. were insoluble, samples of Ariba Machala, and Bahia cocoa beans, without shell, had only 23.2, 22.8, and 19.3 indigestible, and the same beans roasted 39.7, 40.3, and 40.3. O. H.

**On Certain Points in the Estimation of Barium as the Sulphate.** F. W. Mar (*Journal of Analytical and Applied Chemistry*, vol. v., p. 278).—The author finds, as is well known to most analysts, that barium sulphate comes down in a strongly hydrochloric acid solution in a much more granular and filterable condition than from a slightly acid one. He studied the influence of the acidity on the solubility of the sulphate. From a solution containing in 400 c.c. 0.5 gramme barium chloride and amounts of hydrochloric acid varying from 1 c.c. to 5 c.c. the barium was precipitated by means of 10 c.c. dilute sulphuric acid with 10 c.c. to 15 c.c. of hydrochloric acid. The precipitate settled clear in ten to twelve minutes, and was in excellent condition for filtration. The loss under these circumstances amounted to only about 0.4 milligramme.

It is well known that barium sulphate is very apt to carry down with it considerable quantities of alkaline salts, from which it must be purified, generally, by heating with hydrochloric acid after ignition of the precipitate. The author gives the results of a number of experiments in which he dissolved the barium sulphate by heating it with strong sulphuric acid in a porcelain basin, then driving off the acid over a small argand flame, when sandy crystals of barium sulphate are obtained, which are perfectly free from alkaline salts, and can readily be washed and weighed. O. H.

**On the Iodine Number of Lard-Oil by the Hübl Method.** Reuben Haines (*Journal of Analytical and Applied Chemistry*, vol. v., p. 287).—Three samples of lard, stated to be pure, were examined. Two of these were factory lards, and had a melting point of 45°C., whilst a country lard melted at 33°C. The iodine numbers of these samples were 62.30, 62.49, and 59.33 respectively. The oil was then pressed out of the samples by means of a hand drug-press, at a temperature between 45°C. and 65°C. The oils thus obtained began to solidify at about 45°C. Their iodine numbers were 74.14, 73.03, and 70.01; average for oil from both factory lards, 74.0; average of the three, 72.7. The free fatty acid amounted to 0.86, 0.49, and 1.35. The samples gave no silver reaction.

A sample of prime lard-oil, guaranteed by the dealer to be pure, had an iodine number of 74.0, and a Maumené of 42, the experiment being made in the manner recommended by Allen. O. H.

**Detection of Rosin Oil in Fatty and Mineral Oils.** A. Grittner (*Zeit. für angewandte Chemie*, May, 1891).—The author of the paper describes a series of test experiments undertaken with a view to ascertain the sensibility of several processes which have been proposed for this purpose.

He finds the original process proposed by Storch (*Ber. Öst. G.*, 1887, p. 93) has only a limited application; since when the oil is dissolved in acetic anhydride and sulphuric acid added, train oil gives a red colour, and the cholesterin present in many fatty oils produces a violet one. With dark-coloured mineral oils, the violet colour produced by the sulphuric acid is completely masked by the deep colour of the oil. This process was modified by Morawsky, who, instead of adding strong sulphuric acid to the solution of oil in acetic anhydride, used an acid of 1.53 s.g. The colour produced is the same as with the original method of Storch—a violet red. Holde (*M. Vers. Berlin*, 1888, p. 88), used originally an acid of 1.53 s.g., with which rosin oil gives a red colour; later (*Loc. Cit.*, 1890, p. 19.) he increased the strength of his sulphuric acid to 1.624 s.g., since he found that with some rosin oils the colour was only produced with the weaker acid after prolonged shaking. The rosin oils examined by the author gave Morawsky's original reaction, and Holde's original and modified one, the only difference being that, with Holde's stronger acid, the colour appeared immediately, whilst with the weaker acid it was necessary to shake for some time before the colour appeared. Quite black rosin oils did not give Morawsky's reaction so characteristically as was observed with lighter coloured oils. In mixtures of rape and rosin oils in varying proportions the limit of sensibility of Holde's original and modified processes was found to be about 1 per cent.; whilst with Morawsky's process  $\frac{1}{2}$  per cent. could be detected with certainty.

If rape oil be shaken with sulphuric acid of 1.53 s.g. the colour of the deposited acid is little altered, at most to a pale yellow; but if the same oil be treated with acid of 1.624 s.g., the acid is coloured dark yellow. With mixtures of up to 1 per cent. of rosin oil, the 1.53 s.g. acid gives a red colour, whilst the 1.625 s.g. acid gives an orange red one. The author prefers the colour produced by the weaker acid, as being the more characteristic one. Train oils before being tested for rosin oil must be shaken out with alcohol; the alcoholic solution when settled can then be tested for rosin oil. The reaction will be best observed by allowing the sulphuric acid to trickle down the side of the vessel; if rosin oil be present, a red or violet ring will be formed at the place of contact. The author finds with light-coloured train oils mixed with a small percentage of rosin oil Morawsky's method is the preferable one; with dark-coloured oils Holde's method is the best. Morawsky's method is inapplicable in the case of the dark mineral oils used for lubrication purposes. Since resins—colophony, shellac, etc, give a similar reaction, the absence of these bodies must be ascertained. In such cases it is necessary to saponify the oil, and to test the unsaponifiable portion.

For dark mineral oils it is advisable to use sulphuric acid of 1.53 s.g., which, at most gives a slight yellow colour; many mineral oils treated with a stronger acid give a dark yellow colour, which interferes with the sharpness of the reaction. The author considers the method with acid of 1.53 the preferable one; the rosin oils investigated by him gave the reaction just as sharply with the weaker acid as with the stronger.



The author now investigated the action of syrupy phosphoric acid on train and mineral oils. Schoedler\* states that train oil mixed with syrupy phosphoric acid 5 to 1, gives a red colour passing into dark red, which is readily observable in dilutions of 1 per cent. The author denies this, since he obtained not a red, but a dirty brown colour, and this even only after prolonged shaking. Train oils, of undoubted origin, treated with syrupy phosphoric acid, prepared exactly according to Schällen's directions, show only a very weak red colour, which does not increase on prolonged shaking. Holde obtained with rosin oil and phosphoric acid an orange to blood-red colour; the rosin oils, investigated by the author, however, gave colours varying from violet-red to brown-red. Since the colours produced with phosphoric acid are different, no qualitative reaction can be based upon them; nevertheless the author has determined its sensibility.

In mixtures of rosin oil with rape or mineral oils, it was found that sometimes 5 per cent. could be detected; at other times it could not; the difference evidently depending upon the quality of the rosin oil. The phosphoric acid process is therefore very much inferior to those of Morawsky or Holde. W. J. S.

**The Iodometric Estimation of Nitric Acid in Nitrates.** George McGowan (*Jour. Chem. Society*, July, 1891, p. 530).—This process is similar in principle to the one described by De Koninck and Nihoul (*Zeit. f. angew. Chemie*, August 15, 1890), but the details of the method and the apparatus employed are very different.

When a fairly concentrated solution of a nitrate is warmed with an excess of pure, strong hydrochloric acid, the nitrate is completely decomposed according to the following equation:  $\text{—HNO}_3 + 3\text{HCl} = \text{NOCl} + \text{Cl} + 2\text{H}_2\text{O}$ , the chlorine being evolved quantitatively.

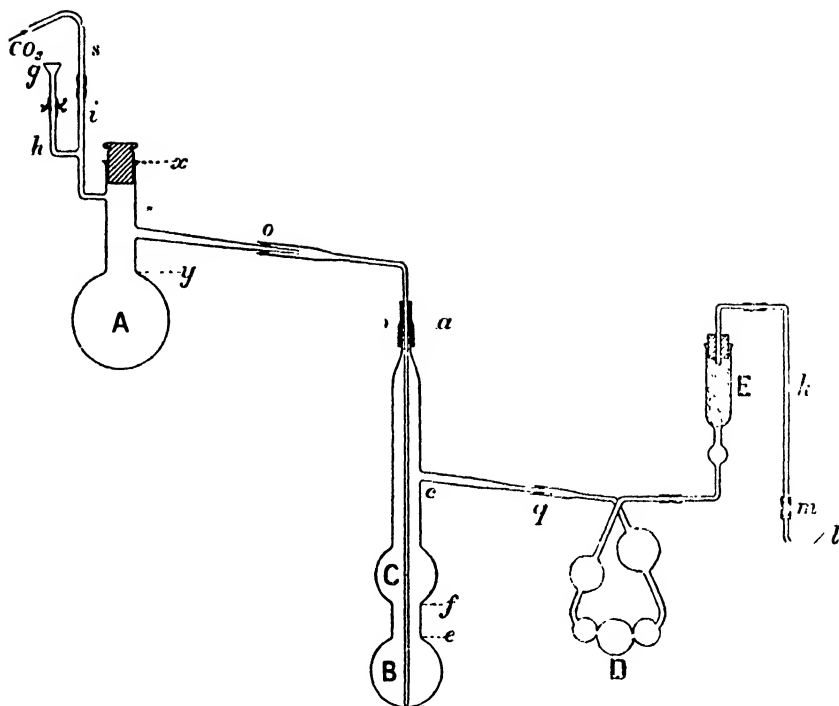
If the operation is conducted in an atmosphere of carbonic dioxide, and the escaping gases are passed through a solution of potassium iodide, an amount of iodine is liberated exactly equivalent to the whole of the chlorine present (free and combined), nitric oxide escaping. One molecule of nitric acid thus yields 3 atoms of chlorine or iodine. The iodine is titrated in the usual manner with sodium thiosulphate.

Absolute exclusion of air from the apparatus is necessary, since if present the nitric oxide would be oxidised to higher oxides of nitrogen, which would liberate a further quantity of iodine.

The following is a description of the apparatus used:—The main point to be attended to is to have no corks or rubber stoppers, etc., for the escaping chlorine to act upon. The form of the apparatus is shown in the accompanying cut; the condensing arrangement for the chlorine works perfectly, and may be used with advantage in other analytical processes in which iodine is set free. The measurements given are those of a conveniently-sized apparatus.

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\* *Unters. der Fette und Oele*, 1890, p. 117.



A is a small, round-bottomed flask, into the neck of which a glass stopper *x* is accurately ground. The capacity of the bulb is about 46 c.c., and the length of the neck, from *x* to *y*, 90 mm. The first condenser is a simple tube, slightly enlarged at the foot into two small bulbs (compare Sutton's "Volumetric Analysis," fourth edition, p. 103). The capacity of the bulb (B) is 25 c.c., and the total capacity of the two bulbs and tube, up to the top of C, 41 c.c. This condenser is immersed, up to the level of *c*, in a beaker, full of water. D is a Geissler bulb apparatus (Dittmar's modification), and E a chloride of calcium tube, filled with broken glass; *g* is a small funnel, attached by rubber and clip to the branch T-tube *h*; between the T-tube (*i*) and the wash-bottle for the carbonic dioxide is placed a short piece of glass tubing (*s*), containing a strip of filter paper, slightly moistened with iodide of starch solution. This tube (*s*) is hardly necessary, as no chlorine escapes backwards if a moderate current of carbon dioxide is kept passing. The joints (*o*, *p*, *q*), of narrow india-rubber tubing, practically expose no rubber to the action of the chlorine; *k* is the outlet tube.

The actual operation is performed as follows:--The nitrate (say, about 0.25 gramme potassium nitrate) is introduced into the clean and dry evolution-flask, 1–2 c.c. water added, the bulb gently warmed to dissolve nitrate, and stopper firmly inserted in flask. About 15 c.c. of a solution of potassium iodide (1 to 4) are run into the first condensing tube, any iodide adhering to the upper portion of the tube washed down with a little water; 5 c.c. iodide solution mixed with 8–10 c.c. water are sucked into the Geissler bulbs; the broken glass in E is thoroughly moistened with the iodide. The Geissler bulbs are arranged so that gas only bubbles through the last of them.

All the joints being tight, the carbon dioxide is turned on briskly until all air is removed from the apparatus. The small outlet tube (*l*) is now replaced by a chloride of calcium tube, filled with broken glass moistened with the above iodide solution, and closed by a cork through which an outlet tube passes, the object of this "trap" being to prevent any air getting back into the apparatus, and a brisk current of carbon dioxide again passed. The stream of gas is now stopped for an instant, and about 15 c.c. pure, chlorine-free hydrochloric acid run into A through the funnel *g* (into the tube of which it is well to have run a few drops of water to displace air), and A is shaken to mix its contents thoroughly. A slow current of carbon dioxide is now turned on (1—2 bubbles through the wash-bottle per second), and A is gently warmed. It is distinctly advantageous that the reaction does not begin until the mixed solutions are warmed, when the liquid becomes orange-coloured, the colour again disappearing after the nitrosyl chloride and chlorine have been expelled. The warming should be very gentle at first to make sure of the conversion of all the nitric acid, and also because the first escaping vapours are relatively very rich in chlorine; afterwards the liquid in A is briskly boiled. When the volume of liquid in A has been reduced to about 7 c.c. or so (by which time it is again colourless), the stream of carbonic dioxide is slightly quickened, and the apparatus allowed to cool down a little. About 2 c.c. of warm hydrochloric acid are run in gently through *g*; there is no fear of the iodide solution running back, or of any bubbles of air escaping through *y* if this be done carefully. The carbon dioxide is once more turned on slowly, and the liquid in A boiled until reduced to about 5 c.c. It is now only necessary to allow the apparatus to cool down, passing carbon dioxide all the time, after which the contents of the condensers are transferred to a flask and titrated with sodium thiosulphate. At the end of a properly-conducted experiment, the glass in the upper part of E should be quite colourless, and there should be only a mere trace of colour in the lower part; the liquid in the last bulb of the Geissler apparatus ought to be only pale yellow. During the operation it is well to test the stopper and also various joints for tightness with a piece of iodide of starch paper; also, before disjoining, to test the gas escaping at *m*, to make sure that all nitric oxide has been expelled.

The following test experiments are given:—Of finely-powdered pure potassium nitrate, dried at about 160°C.\*, 0.2627 gramme gave 0.2624 gramme, or 99.89 per cent. 0.2990 gramme gave 0.2992 or 100.08 per cent.

An analysis of a commercial nitrate of soda gave the following results:—

|                                 |    |    |    |    |    |                |
|---------------------------------|----|----|----|----|----|----------------|
| Moisture at 160°C.              | .. | .. | .. | .. | .. | 2.95 per cent. |
| NaNO <sub>3</sub>               | .. | .. | .. | .. | .. | 94.68 " "      |
| NaCl                            | .. | .. | .. | .. | .. | 1.55 " "       |
| Na <sub>2</sub> SO <sub>4</sub> | .. | .. | .. | .. | .. | 0.44 " "       |
| Insoluble matter (ignited)      | .. | .. | .. | .. | .. | 0.44 " "       |

100.06

The author made a number of experiments with the addition of manganese

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\* The author finds the moisture of commercial nitrate of soda is not completely driven off at the temperature of an ordinary air (water?) bath (about 95°C.).

sulphate as an intermediary; and though fairly accurate results were obtained in this way, he finds the process acts better without any addition of this kind.

The process is only applicable in the absence of organic matter and reducing agents generally. There are two slight errors involved in it which neutralise one another—the difficulty of getting rid of the last traces of air in the carbon dioxide generated in a Kipp apparatus, and the slight loss by volatilisation of iodine in transferring the iodide liquid to the flask for titration. A strong solution of potassium iodide should therefore be used. The nitric oxide is apparently completely driven out of the apparatus in a properly conducted experiment. The presence of nitric oxide in the fluid to be titrated may be readily detected by the blue colour returning immediately after the solution has been decolourised by thiosulphate. A fifth-normal thiosulphate solution (50 grammes per litre) was found the most convenient strength to work with, 0.25 potassium nitrate requiring about 38 c.c. of such a solution. Advantages of the process are:—rapidity and simplicity.

W. J. S.

**Determination of Nitrates in Water.** A. Hazen and H. W. Clark (*Journ. of Anal. and Applied Chem.*, Vol. v., p. 301).—The phenol-sulphonic acid process, which essentially consists in the evaporation of a measured portion of the water to dryness, treating the residue with a solution of phenol in sulphuric acid and rendering the solution strongly alkaline, the yellow colour produced being compared with that obtained in a similar manner from a known quantity of nitric acid, was carefully investigated. The best results are obtained with about 1 c.c. of a 5 p.c. solution of strictly pure phenol in sulphuric acid, nearly free from water, added to the residue and without warming. Caustic soda was substituted for ammonia for rendering alkaline.

Attempts to use standards made from pure picric acid proved entirely unsuccessful, the colour being only one-third as deep as that made by treating potassium nitrate with phenol-sulphonic acid. Other nitro-phenols were tried, but none matched the standards perfectly. It was recognised that in the solutions prepared from potassium nitrate, a mixture in varying proportions of different nitro-phenols was obtained. These have not the same colour for equal contents of nitrogen, and the authors were unsuccessful in so controlling the reaction as to get a constant product, or in finding a substituted phenol with which there can be only a single nitro-compound sufficiently soluble in water or otherwise adapted for the purpose. The results of the process upon 150 ground waters averaged 11 p.c. lower than the results obtained by reduction by the aluminium method. In some instances the chlorine was removed from the water with silver sulphate; although the results in these cases were somewhat higher, yet they were deficient. The authors conclude, that while the process may be useful in some cases, the results generally are not of the requisite accuracy.

O. H.

**Volumetric Estimation of Phenol.** Meissinger and Wortmann (*Pharm. Zeit. f. Russland*, xxix., p. 759, through *Journ. de Pharm. Brussels*, Vol. xlvii., p. 244).—The process is based on the property possessed by iodine of combining

with phenol in alkaline solution, in the proportion of 6 atoms I to 1 mol. phenol.

For the analysis 2—3 grammes phenol are dissolved in sodium hydroxide solution (3 eq. NaHO to 1 eq. phenol) and made up to 500 c.c. with water; 10 c.c. of this are placed in a flask, warmed to 60° C., and decinormal iodine added until the solution is faintly yellow, with formation of a red precipitate. When cold, solution is acidified with dilute  $H_2SO_4$ , made up to 500 c.c. and filtered. In 100 c.c. of the filtrate, the excess of I is titrated with decinormal sodium thiosulphate; this amount, deducted from the total I used, gives amount absorbed by phenol, which, when multiplied by 0.123518, gives amount of phenol in sample assayed.

W. J. S.

**The Estimation of Glycerine by the Benedikt-Zsigmondy Method.** C. Mangold (*Zeitsch. f. angew. Chem.*, 1891, p. 400).—The reduction of the excess of permanganate by means of hydrogen peroxide, first proposed by Herbig, is recommended in preference to sodium sulphite, as used by Allen. The author simplifies the method by carrying out the oxidation in the cold. He operates as follows:—0.2 to 0.4 gramme of glycerine are dissolved in about 300 c.c. of water, 10 grammes potassium hydrate and so much 5 per cent. solution of permanganate is added, that for each part of glycerine about seven parts of permanganate are present. The mixture is allowed to stand at ordinary temperature for half an hour. Hydrogen peroxide is then added until the liquid is colourless, well shaken, filled up to one litre, 500 c.c. are filtered off through a dry filter, boiled for half an hour to destroy the excess of peroxide, allowed to cool to about 80°C., and after acidulation with dilute sulphuric acid, the oxalic acid titrated with standard permanganate. The author gives satisfactory test experiments. O. II.

**On Coffee and Rice-Flour Adulteration.** Ed. Maandbl Vervalsch. May, 1891.—The author lately examined a sample of coffee-berries, which the buyer suspected to be an artificial product consisting chiefly of baked dough. There was, however, no mistake about their being genuine coffee, although unusually strongly coloured. As, however, the microscopical examination showed a remarkable freedom from oily globules, the author thought it as well to make a chemical analysis, which clearly proved the berries had been thoroughly exhausted (no doubt to manufacture coffee extract), and afterwards stained.

The same author also again calls attention to the adulteration of rice-flour with carbonate of calcium (marble); one sample containing no less than 56 per cent. of marble.

**ERRATA.**—In the June number, page 120, letter to Editor, for Nitrogen as nitrates, etc. Nitrites read Nitrogen as Nitrates and nitrites, in both places where it occurs.

# THE ANALYST.

SEPTEMBER, 1891.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

### SUMMER MEETING.

A NEW departure was made this year in the arrangements of what has hitherto been known as the Country Meeting of the Society; it being decided to start from London, and to investigate the beauties of the upper reaches of the Thames. Accordingly, some thirty-five members and friends (including a fair amount of ladies), met at Paddington on the morning of the 31st ult., and travelled by rail to Maidenhead. Here they found a well-appointed steam launch in readiness, which conveyed them to Sonning. After dining here, they again embarked, and steamed to Henley, whence town was reached by train. Altogether a most enjoyable day was spent, and it was unanimously agreed by those present that the meeting had been one of the most successful of its kind which had been held in recent years. Some excellent photographs of the party were taken at Sonning by Messrs. Chattaway, Davies, and Stansell.

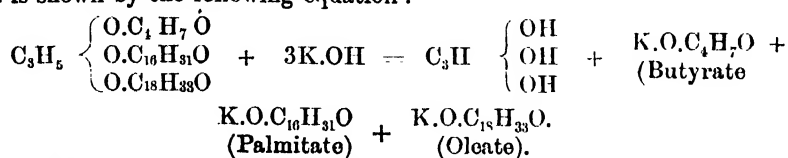
## ON THE CONSTITUTION OF BUTTER FAT.

BY ALFRED A. ALLEN.

(*Read at Meeting, June 3rd, 1891.*)

IN compiling the following notes, my object has not been to offer a complete essay on the constitution of butter-fat, but rather to examine the nature of the evidence on which certain theories of its constitution have been founded, and to refute these theories so far as they have been proved inconsistent with experiment.

When butter-fat is saponified, it is well known to yield butyric acid and other acids which are generally considered as being oleic and palmitic acids, besides smaller amounts of arachidic, stearic, myristic, and lower acids of the stearic series. The result of saponifying a complex glyceride molecule containing the radicles of butyric, palmitic, and oleic acids is shown by the following equation:—

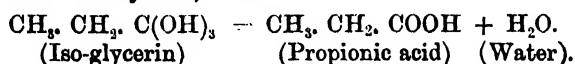


There is good reason for believing that butter-fat contains such complex glycerides as the above, for the butyrin cannot be separated by any process of fractional solution from the less soluble glycerides of the fat.

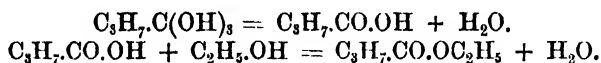
By treating butter-fat with only half the quantity of alcoholic soda necessary for its complete saponification, and precipitating the liquid with water, Dr. James Bell

obtained an oil which solidified at  $4.4^{\circ}\text{C.}$ , and on saponification yielded 88.1 per cent. of insoluble acids, but no butyric or other soluble fatty acids. This result agrees with a diglyceride of the following character, though it is to be regretted that no determination of the glycerin was made:— $\text{C}_3\text{H}_5 : \text{O.H, O.C}_{16}\text{H}_{31}\text{O, O.C}_{18}\text{H}_{35}\text{O.}$

In 1883, Messrs. J. A. Wanklyn and W. Fox enunciated a new theory of the constitution of natural fats (*Chem. News*, xlviii., p. 49; *British Association Reports*, 1883, p. 470; *ANALYST*, IX., p. 73). The theory, which was only shortly stated, was simply that the accepted view that fats are ethers of glycerin is only partially correct, and that instances of a different kind of structure occur among the natural fats and oils. According to the authors of the theory, the fats are, in fact, composed of ethers of iso-glycerin or homologues of iso-glycerin. To the wholly hypothetical compound iso-glycerin, the authors assign the formula:— $\text{CH}_3.\text{CH}_2.\text{C}(\text{OH})_3$ . This theoretical compound is assumed to exist only in its ethers, for immediately on isolation it is imagined to be resolved into water and a fatty acid, thus:



Of the existence of the iso-glycerin with 3 carbon-atoms absolutely no evidence has been attempted to be given; but the authors consider that proof of the existence of ethers of the next higher homologue in butter-fat is afforded by the formation of ethyl butyrate when the fat is treated with an amount of alcoholic potash insufficient for its complete saponification. The formation of the ethyl butyrate they attribute to the decomposition of an iso-glycerin containing  $\text{C}_4$ , this iso-glycerin splitting up into butyric acid and water, and the nascent butyric acid reacting with the alcohol to form ethyl butyrate, thus—



Wanklyn and Fox found that under favourable conditions they could obtain from butter-fat an amount of ethyl butyrate equivalent to fully 3 per cent. of butyric acid, or about one-half of the total amount which can be isolated from saponified butter. Upon this single fact, coupled with an alleged serious deficiency in the amount of glycerin yielded when fats, and especially butter-fat, are saponified, the authors erected their iso-glycerin theory. But the reaction in question was some years since demonstrated by Mr. Hehner to be true also of synthetically prepared glyceryl butyrate; besides which I believe the authors of the theory have never published a single original experiment in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibits any grave departure from the amount required by the accepted view of their constitution. In view of this omission on the part of the authors to support their position by experiment, the iso-glycerin theory might well have been allowed to remain at rest, had it not recently been resuscitated by Mr. Wanklyn in a wholly unaltered form. Thus on a recent occasion Mr. Wanklyn stated that "the evidence of the existence of the isoglyceride was that reaction (*i.e.*, the formation of ethyl butyrate) and the fact that one did not get the theoretical quantity of glycerin from butter." From this concise statement of his views it would appear that Mr. Wanklyn has forgotten Mr. Hehner's destruction of his one supporting

experiment, and is ignorant of, or ignores the fact that since the original enunciation of the theory, other chemists have supplied his omission and determined the glycerin resulting from the saponification of a number of fats and by a variety of methods.

Mr. Wanklyn considers that the formation of ethyl butyrate on heating butter-fat with a limited quantity of alcoholic potash proves the presence of an isoglyceride, the iso-glycerin of which splits up into butyric acid and water, the acid reacting with the alcohol to form ethyl butyrate. He contends that if the butyric acid were a primary product of the saponification of an ordinary glyceride, instead of a secondary product of the decomposition of an iso-glycerin, it would not form ethyl butyrate, but potassium butyrate. It is certainly a curious and interesting fact that ethyl butyrate should be formed under these circumstances, seeing that it is readily converted by caustic potash into alcohol and potassium butyrate. But it must be remembered that the essential condition of its formation in notable amount, prescribed by Wanklyn and Fox themselves, is the use of the alkali in quantity insufficient to saponify the whole of the butter-fat employed. The whole argument of the reaction falls to the ground in the face of the fact, demonstrated by Mr. Hehner under the very noses of Messrs. Wanklyn and Fox, that butyric acid synthetically prepared by heating together butyric acid and glycerin, and thoroughly washing the product, develops abundance of ethyl butyrate when warmed with alcoholic potash!

The fact is that the reaction which is regarded by Mr. Wanklyn as so anomalous appears to be a perfectly normal and general one. Thus ethyl stearate may be actually prepared by boiling tristearin with solution of sodium in absolute alcohol (Duffy), or *by heating tristearin with small quantities of alcoholic potash* (Bouis, *Comp. Rend.* xlv. p., 35). Herewith is the precise condition of success in obtaining ethyl butyrate applied by Bouis to prepare the higher homologue. P. Duffy (*Jour. Chem. Soc.* v., p. 303), also obtained amyl stearate by boiling tristearin with a solution of sodium in amyl alcohol, and amyl palmitate by precisely similar means. When in the reaction of stearin and palmitin with amylate of sodium the proportion of the latter "was increased beyond one equivalent, the quantity of ether obtained diminished," and "with a quantity of sodium which was certainly not less than two equivalents, no ether was obtained."

It appears, therefore, that Mr. Wanklyn has merely re-discovered with respect to butter what was pointed out in the case of stearin and palmitin in 1853.

Duffy determined the glycerin produced by the saponification of the stearin he employed. The method of estimation consisted in evaporating the neutralised liquid resulting from the saponification nearly to dryness at a steam heat, adding dry potassium carbonate, extracting the glycerin with absolute alcohol, filtering the solution, and evaporating the filtered solution in a vacuum until the residue was constant in weight. The glycerin thus found was corrected by the deduction of the ash left on ignition. By this process, which is likely to give low results, Duffy obtained 8.94 per cent. of glycerin in two experiments, the theoretical yield from pure stearin being 10.34 per cent., a figure which does not leave Mr. Wanklyn much margin for the suggestion that the ethyl and amyl stearates were derived from an iso-glycerin, which, under the circumstances, would have to be the member with 18 carbon atoms.

The process of estimating glycerin employed by Duffy is substantially the same as



that described by Chevreul in 1823, by which that chemist isolated the following proportions of ash-free glycerin:—Human fat, 9.66 per cent.; pork, 8.82; beef, 8.60; mutton, 8.00; butter-fat, 11.85; porpoise oil, 14.00. These results, with the exception of the two last, are sensibly below the theoretical yield, as might be expected from the process employed. Further, the statement made by Mr. Wanklyn that manufacturers never obtain more than 5 per cent. of glycerin on saponifying fats, is contrary to the experience of some of the largest firms, who *recover* 7.5 to 8 per cent., and take no notice of the considerable loss of glycerin by evaporation during the process of concentration; besides which the process of saponification is often far from complete.

To come to more recent determinations of glycerin in fats, Mr. Hohner has published the following figures, obtained by boiling the leys from the saponification with a dilute acid solution of potassium bichromate and ascertaining the excess of oxidising agent by titration with a ferrous salt (ANALYST xii., p. 44).

Now this process is not open to the objection which has been raised against some, for it has been recently stated by Mr. Wanklyn's coadjutor (*Jour. Soc. Chem. Ind.*, x., p. 204), that dilute chromic acid mixture remained practically unchanged when boiled with butyric acid, and, further (ANALYST xvi., p. 30), that butyric acid is the only soluble non-volatile fatty acid to be detected in the glycerin mother-liquor obtained by the saponification of butter-fat.

The following are figures obtained by Mr. Hohner by the bichromate titration process:—

| Fat.                  | Glycerin.       |
|-----------------------|-----------------|
| Olive oil .. .. .     | 10.26 per cent. |
| Cod-liver oil .. .. . | 9.87 „ „        |
| Linseed oil .. .. .   | 10.24 „ „       |
| Margarine .. .. .     | 10.01 „ „       |
| Butter-fat .. .. .    | 12.40 „ „       |
| Butter-fat .. .. .    | 12.40 „ „       |

As already pointed out, it is a curious fact that the authors of the iso-glyceride theory have not, to my knowledge, published any experiments in support of their assertion that butter, tallow, and other fats yield on saponification little more than half the theoretical proportion of glycerin. This is the more curious since a valuable method of determining glycerin in fats was originally suggested by Mr. Wanklyn, and further worked out by Mr. Fox (*Oil and Colour Jour.* v., p. 1,402; *Chem. News*, liii., p. 15), and Benedict and Zsigmondy (*Chem. Zeit.* ix., p. 975, ANALYST x., p. 206). The method is based on the oxidation of the glycerin by treatment with permanganate in presence of excess of caustic alkali, whereby it is converted into oxalic acid, carbon dioxide, and water, in accordance with the equation:— $C_3H_5O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O$ . The excess of permanganate is destroyed by a sulphite, the filtrate acidulated with acetic acid, and the oxalate precipitated as a calcium salt. The process has been very thoroughly investigated in my laboratory by Mr. J. C. Belcher, and proved to give very accurate results in the absence of foreign bodies yielding oxalic acid by oxidation. Alcohol is one of these, and hence to avoid all risk of its presence I have described a method of saponifying the substance with aqueous potash (ANALYST xi., p. 52; *Com. Org. Analysis* ii., p. 290). This modification, and careful proof by experiment that oxalic acid is not acted

on by permanganate in strongly alkaline solution, is the extent of my responsibility for the process in question. Benedict and Zsigmondy, however, proved by experiment that the soluble fatty acids of oils, such as acetic, butyric, caproic, etc., do not, on treatment with alkaline permanganate, yield any acids, the calcium salts of which are precipitated from acetic solutions, and hence are liable to be mistaken for calcium oxalate. The higher fatty acids of the stearic series are insoluble in water, and hence would not in any case interfere. On the other hand, certain acids of the oleic and acrylic series, and possibly oleic acid itself, yield oxalic acid by oxidation with permanganate. The higher acids of the oleic series are, however, insoluble in water, and the lower are not known to occur in fixed oils under normal conditions. Under certain circumstances, however, the method is wholly invalidated, as I found when attempting to apply it to the examination of oxidised linseed oil.

The following tabulated statement of results obtained by the alkaline permanganate process of estimating glycerin is taken from vol. ii. of my *Commercial Organic Analysis*, p. 33 :—

| Kind of fatty oil.                   | Glycerin per cent.      |              |
|--------------------------------------|-------------------------|--------------|
|                                      | Benedict and Zsigmondy. | A. H. Allen. |
| Northern whale oil .. .. .           | —————                   | 11·96        |
| Porpoise oil .. .. .                 | —————                   | 11·09        |
| Menhaden oil .. .. .                 | —————                   | 11·10        |
| Lard .. .. .                         | —————                   | 10·83        |
| Tallow .. .. .                       | 9·9 to 10·0             | —            |
| Butter-fat .. .. .                   | 10·2 to 11·6            | 11·06        |
| Olive oil .. .. .                    | 10·1 to 11·4            | —            |
| Linseed oil .. .. .                  | 9·4 to 10·0             | 9·39         |
| Castor oil .. .. .                   | —————                   | ·13          |
| Cocoa-nut oil .. .. .                | 13·3 to 14·5            | 12·11        |
| Palm-nut oil .. .. .                 | —————                   | 11·70        |
| Palm oil (containing much free acid) | —————                   | 9·71         |

The applicability of the alkaline permanganate process to the estimation of glycerin from butter has been recently denied (*Chem. News* xvi., p. 49, *Jour. Soc. Chem. Ind.* x., p. 204, *ANALYST* xvi., p. 49) on the ground that butyric acid itself yields oxalic acid on treatment with alkaline permanganate in the manner described by Benedict and Zsigmondy for the estimation of glycerin. The same authority states (*ANALYST* xvi., p. 30) that butyric acid is the only soluble non-volatile acid he could detect in the glycerin mother-liquor from the saponification of butter, and he also states that the oxalic acid yielded is equivalent to 11·7 to 12·23 per cent. of glycerin (*Jour. Soc. Chem. Ind.* x., p. 93). The effect of alkaline permanganate on butyric acid is alleged to be to oxidise it to oxalic acid in accordance with the following eccentric equation (*Chem. News* lxiii., p. 111, *Jour. Soc. Chem. Ind.* x., p. 204):— $C_4H_8O_2 + O_3 = 2C_2H_2O_4 + H_4$ .

The discoverer of this reaction quotes two experiments on pure butyric acid by which he obtained amounts of oxalic acid corresponding to 93·64 and 94·07 per cent. of the butyric acid taken. This result is of so startling and remarkable a nature, and so completely opposed to the experience of Benedikt and Zsigmondy and all previous observers, that it is naturally received with some reserve, especially as the observer recently published experiments (*ANALYST* xvi., p. 26) according to which tallow requires

23 per cent. of caustic potash (KHO) for its saponification against 19.3 to 19.8 per cent., which is the united experience of numerous other observers; that butter-fat requires about 27 per cent. of potash, against the general experience of 21.1 to 23.3 per cent; and detailing other analytical results of an equally remarkable character.

As, however, the observer in question makes the distinct assertion, as the result of experiment, that butyric acid is oxidised to oxalic acid by alkaline permanganate, and hence that the estimation of glycerin in butter by the same process is invalidated, and considerable support thereby given to Mr. Wanklyn's iso-glyceride theory (*Jour. Soc. Chem. Ind.* x., p. 204), I have thought it right to ascertain by personal experiment whether the statement in question had any foundation in fact. That the assertion was baseless was already rendered extremely probable by Mr. Hehner's failure to obtain any trace of oxalic acid from butyric acid by treatment with permanganate (ANALYST xvi., p. 49).

In order to settle the point beyond the possibility of further cavil, I saponified 20 grammes of Kiel butter-fat by heating it for six or eight hours at 100° C. in a closed bottle, with a solution of 8 grammes of caustic potash in 50 c.c. of water. The soap obtained was dissolved in hot water and decomposed by dilute sulphuric acid in quantity sufficient to convert the potash into  $\text{KHSO}_4$ . The liquid was then allowed to become cold and poured off through a filter from the cake of insoluble acids. The latter was washed by boiling with water, the washings when cold being added to the main solution. This solution, containing the glycerin and soluble fatty acids resulting from the saponification, was then distilled to a small bulk, water added, and the liquid again distilled to a small volume.

The distillate was then oxidised by alkaline permanganate in the usual way. The reduced and filtered liquid gave no trace of precipitate when acidulated with acetic acid and treated with calcium chloride, showing that no oxalic acid had been formed from the butyric acid, and that no glycerin had distilled over.

The residual liquid remaining in the distilling flask was divided into four equal portions. Nos. 1, 2 and 3 were oxidised, respectively, by a slight excess, a moderate excess, and a large excess of alkaline permanganate, by which quantities of oxalic acid were found equivalent respectively to a production of 11.12, 11.52, and 11.78 per cent. of glycerin by the saponification of the butter-fat. The fourth portion of the liquid was exactly neutralised by caustic potash, and filtered from the potassium sulphate which crystallised out. The filter was washed with alcohol, and more alcohol added to the filtrate as long as a precipitate was produced. The liquid was filtered and evaporated on the water-bath till the residue was nearly constant in weight. The residue, which was syrupy and had the characters of glycerin, was ignited and the ash deducted from the weight previously observed. A direct determination of the glycerin by weight, in this manner, showed 11.22 per cent.

Other estimations of glycerin by the same process, but employing 20 grammes (instead of 5 grammes) of butter-fat gave 10.77, 11.53, and, 12.15 per cent. of ash-free glycerin.

In another experiment, 20 grammes of butter-fat were saponified with aqueous

potash, the soap decomposed with acid, and the acid liquid divided into two equal portions, A and B.

|  |   |  |                 |
|--|---|--|-----------------|
| A was distilled to a small bulk as before, and the residue in the flask divided into two equal portions. |   | B was divided into two equal parts without previous distillation to separate butyric acid. |                 |
| No. 1 showed by the oxidation with alkaline permanganate 11.52 per cent. of glycerin.                    | No. 2 gave Mr. Hehner by the bichromate oxidation method 11.83 per cent. of glycerin. | No. 3 showed with alkaline permanganate 10.86 per cent. of glycerin.                       | No. 4 was lost. |

The foregoing experiments were made in my laboratory by Mr. D. Homfrey, to whom my best acknowledgments are due. The experiments appear to prove:—

1. That butyric acid does not yield oxalic acid when oxidised by alkaline permanganate in the manner prescribed by Benedikt and Zsigmondy.

2. That the amount of oxalic acid produced by the treatment of the soluble products of the oxidation of butter by alkaline permanganate is not greater when the oxidation is effected in the presence of the butyric acid than when the acid is previously removed by distillation.

3. That the oxalic acid produced by the permanganate treatment corresponds to a formation of 11 or 12 per cent. of glycerin from the butter-fat saponified.

4. That this result is fully confirmed by actual isolation and weighing of the glycerin from the saponification.

5. That there is no foundation for the iso-glyceride theory so far as butter-fat is concerned.

#### NOTE ON THE REACTION OF ACETIN WITH ALCOHOLIC POTASH.

By A. H. ALLEN AND D. HOMFREY.

SINCE the paper on "The Composition of Butter-fat" was read by one of us at the June meeting of the Society of Public Analysts, we have made some experiments with a view of ascertaining whether glyceryl acetate (acetin) behaved with alcoholic potash in a manner similar to glyceryl butyrate (butyrin); in other words, whether on heating acetin with a quantity of alcoholic potash insufficient for its complete saponification a notable amount of ethyl acetate (acetic ether) could be produced.

Some acetin was prepared by heating together 5 parts of glycerin with 6 of anhydrous sodium acetate and 15 of acetic anhydride. The mixture was kept boiling for an hour in a flask furnished with a reflux condenser. It was then treated with water, and sodium carbonate added till the reaction was permanently alkaline, when the liquid was shaken with ether, which was separated, and the acetin recovered by distilling off the solvent.

One gramme of the acetin thus prepared was distilled with 30 c.c. of alcohol and 0.5 c.c. of alcoholic potash containing 80 grammes of caustic potash per litre. The distillate, which smelt strongly of acetic ether, was heated on the water-bath for half-an-hour with 10 c.c. of the same alcoholic potash solution ( $\approx$  11.8 c.c. normal KHO), and the excess of alkali titrated back with standard hydrochloric acid and phenolphthalein in the usual way. From this result we calculated the weight of acetic acid volatilised as acetic ether. The residue in the retort was treated with more alcohol and another 0.5 c.c. of alcoholic potash, the liquid distilled, and the distillate saponified as before. The following results were obtained, operating on one gramme of acetin in each case:—

|                   |    | Alcoholic KHO<br>employed. |    | Acetic Acid<br>in distillate. |    | Acetin. |
|-------------------|----|----------------------------|----|-------------------------------|----|---------|
| A. 1st Distillate | .. | 0.5                        | .. | 53.4 %                        | .. | 65.12 % |
| 2nd Do.           | .. | 0.5                        | .. | 17.4 „                        | .. | 21.22 „ |
| Total             | .. | 1.0                        | .. | 70.8 „                        | .. | 86.34 „ |
| B. 1st Distillate | .. | 0.2                        | .. | 43.8 %                        | .. | 53.41 % |
| 2nd Do.           | .. | 1.0                        | .. | 26.4 „                        | .. | 32.19 „ |
| Total             | .. | 1.2                        | .. | 70.2 „                        | .. | 85.60 „ |

The theoretical yield of acetic acid, supposing the whole of the substance employed to be pure triacetin and the conversion into ethyl acetate to have been complete, would be 0.826 against 0.708 and 0.702 grammes actually produced.

A fresh quantity of acetin was next prepared, and an experiment made to ascertain if it volatilised with alcohol. 1.0848 gramme of acetin was distilled over with 50 c.c. of alcohol, the distillate and residue both saponified, and the acetin calculated as before. In the distillate only 0.015 of acetic acid was found, while the residue contained 0.752 gramme, the sum of the two being 0.767 gramme. This result shows that the extraordinary results previously obtained were not due to actual volatilisation of acetin as such. The total yield of acetic acid is below the theoretical amount (0.826 gramme) doubtless owing to the presence of mono- or di-acetin in the material employed. That it was not due to any error of experiment was proved by saponifying a known weight of the acetin with excess of alcoholic soda ( $\frac{N}{5}$  normal) under a reflex condenser, and ascertaining the alkali consumed in the reaction by titration with standard acid and phenolphthalein in the usual way. A yield of 76.03 per cent. of acetic acid was obtained, as against 76.7 recorded above.

Another experiment was then made by distilling 1.135 gramme of the same specimen of acetin with 1.0 c.c. of  $\frac{N}{5}$  normal soda and 30 c.c. of alcohol. The distillate was saponified with a known quantity of the same alcoholic soda and titrated back with hydrochloric acid as usual. The residue in the retort was again distilled with alcohol and 1.0 c.c. of the same soda solution, and this treatment was repeated once more. The following are the figures obtained:—

|                |    | Alcoholic NaHO<br>employed. |    | Acetic Acid<br>in distillate. |    | Acetin. |
|----------------|----|-----------------------------|----|-------------------------------|----|---------|
| 1st Distillate | .. | 1.0                         | .. | 32.19 %                       | .. | 39.02 % |
| 2nd Do.        | .. | 1.0                         | .. | 26.22 „                       | .. | 31.97 „ |
| 3rd Do.        | .. | 1.0                         | .. | 11.00 „                       | .. | 13.41 „ |
| Total          | .. | 3.0                         | .. | 69.41 „                       | .. | 84.40 „ |

The volume of the caustic soda solution requisite to completely saponify the 1.135 gramme of acetin employed would be 50 c.c. Hence 1 c.c. of the alkaline solution is chemically sufficient to saponify only about one-fiftieth of the acetin used, and yet it causes the conversion of 39 per cent. of it into acetic ether, while 3 c.c. converts the large proportion of 84.4 per cent.

It seems desirable to place these remarkable results on record, but we refrain for the present from attempting any explanation of the curious reaction in question.

Two supplementary experiments deserve mention. 1 gramme of anhydrous sodium acetate was distilled with 50 c.c. of alcohol, the distillate boiled with alkali and titrated with standard acid, when it was found that no acetic ether had been formed. A mixture of acetin, alcohol, and anhydrous sodium acetate gave a small yield of acetic ether, the acetic acid corresponding to 5.26 per cent. of the acetin employed.

## THE DETERMINATION OF ROSIN IN ITS MIXTURES WITH FATTY ACIDS.

By E. TWITCHELL.

(*Journ. of Anal. and Applied Chem.*, vol. v., p. 379.)

The ethyl ethers of fatty acids, as is well known, are most readily formed by acting on an alcoholic solution of the latter with hydrochloric acid gas, the HCl merely serving to remove the water formed by the combination. This reaction I have found to be practically complete where the alcohol employed is absolute, and the HCl gas is passed to saturation. No other precautions are necessary.

On attempting to etherify resin acids (common rosin) in the same way, I found that no combination takes place between the alcohol and acid, and that when the solution is kept cool the resin acid is entirely unacted on, and can be again separated by diluting with water and boiling to collect the precipitate.

This important difference suggested a method for separating resin from fatty acids, which on being practically applied gave me separations such as, I think, are impossible by any of the methods now in use.

The analysis may be either gravimetric or volumetric, and depends on the fact that by the means indicated all the fatty acids are combined to form ethers which are neutral in alcoholic solution and unacted upon by alkalies in the cold, whilst the rosin is left as it was reacts acid in alcoholic solution with phenolphthaleine, and combines easily with caustic potash to form a soluble soap. It is, therefore, simply necessary to effect the combination of the fatty acids with alcohol, when the resin acids may be titrated with standard soda solution, using phenolphthaleine as indicator, or they may be combined with potash, and the rosin-soap thus formed separated from the unsaponified fatty ethers by extracting with naphtha in a separatory funnel.

The gravimetric method is carried out as follows:—2 or 3 grammes of the mixture of fatty acid and rosin are dissolved in ten times their volume of absolute alcohol in a flask, and dry HCl gas passed through in a moderate stream. The flask is set in a vessel with water to keep it cool. The HCl is rapidly absorbed, and after about forty-five minutes, the ethers separate, floating on the solution, and no more HCl is absorbed.

The flask is removed and allowed to stand half an hour longer to ensure a complete combination of the alcohol and fatty acid. It is then diluted with about five times its volume of water and boiled until the acid solution is clear, the ethers, with rosin in solution, floating on top. To this is added some naphtha, and the whole transferred to a separatory funnel, the flask being washed out with naphtha. The acid solution is then run off, and the naphtha solution (which ought to measure about 50 c.c.) washed once more with water, and then treated in the funnel with a solution of 0.5 gramme KHO and 5 c.c. alcohol in 50 c.c. water and agitated. The rosin is immediately saponified, and the two layers separate completely. The solution of rosin soap can then be run off, treated with acid, the rosin collected in any manner desired, dried, and weighed. A second washing of the soap with naphtha is hardly necessary, as very little remains after the first extraction. The naphtha used is 74° gasoline, and for this purpose is much to be preferred to ether.

The first stages of the volumetric method are similar to those of the gravimetric, with the exception that the contents of the flask are washed into the separatory funnel with ether instead of naphtha, and the ether solution in the funnel is then thoroughly washed with water until the wash-water is no longer acid; 50 c.c. alcohol, previously neutralised, are then added, and the solution titrated with standard NaHO solution. If the combining equivalent of rosin is known, its percentage may be calculated, or some of the original mixture may also be titrated, when the difference in NaHO required will correspond to the fatty acids converted into ether.

I have tested this method by a number of experiments, some of which I will here describe. As a first step it was necessary to determine the effect of HCl gas on alcoholic solutions of fatty acid and resin acids separately.

1. Five grammes of distilled fatty acids were dissolved in 50 c.c. absolute alcohol, treated with HCl gas in the manner described, then treated with water, boiled, washed in a separatory funnel, and dried. They yielded 5.451 grammes of ethyl ethers. These ethers were dissolved in neutralised alcohol and titrated with normal solution of NaHO. They required for neutralisation 0.14 c.c. of the solution. This would represent 0.97 per cent. of resin acid, taking 346 as the combining equivalent of rosin, *i.e.*, the weight of rosin neutralised by 1 c.c. normal alkali equal 0.346 grammes.

2. Five grammes fatty acids from a low-grade tallow were treated in the same way, and required 0.06 c.c. for neutralisation, equal 0.41 per cent. resin.

These figures, although not indicating a perfect combination, are still very small, and I think can be explained, especially in the first case, by the supposition that there were actually some resin acids present, natural constituents of the crude fats.

3. Five grammes of an average sample of rosin were treated in exactly the same manner as in working with the fatty acids. After diluting with water and boiling, the rosin was collected by dissolving in a little ether, and found to weigh 4.9382 grammes. This was dissolved in alcohol, and required 14.27 c.c. of the NaHO solution to neutralise it. Five grammes of the original rosin were titrated, and required 14.45 c.c. There had been a slight loss in drying, but no change in the combining weight.

It was found that if the alcoholic solution became heated by the HCl gas, or if the

solution was boiled without first diluting with water, the rosin suffered some change and required less NaHO to neutralise it.

Analyses were made of a number of mixtures. In using the volumetric method, the mean combining weight of fatty acids was taken at 275, and of rosin 346.

A mixture consisting of 20 per cent. rosin, 80 per cent. fatty acids, gave by the volumetric method 20·36 per cent., 21·40, and 19·91 per cent. rosin, the same by the gravimetric method 18·93 per cent. rosin.

A sample of soap said to be made of 100 parts fat to 40 of rosin, and therefore containing 28·67 per cent. rosin, assayed by the volumetric method, 73·7 per cent. fatty acids, and by the gravimetric method 25·7 per cent. rosin.

Unsaponifiable matter in the fat does not affect the process, but can be determined by the volumetric method in one operation, as follows :—Two grammes of the original fatty mixture are titrated with normal NaHO solution and saturate *A* c.c. Two grammes are treated with HCl gas, etc., then titrated and saturate *B* c.c., then  $B \times 0\cdot346$  is the weight of rosin.

$A - B \cdot 0\cdot275$  is the weight of the fatty acids. The remainder is unsaponifiable matter.

A mixture of rosin, fatty acids, and paraffin was prepared and analysed in this manner, with the following results :—

|            |    |    |    |    |    |    | Calculated. | Found. |
|------------|----|----|----|----|----|----|-------------|--------|
| Rosin      | .. | .. | .. | .. | .. | .. | 21·3        | 22·6   |
| Fatty acid | .. | .. | .. | .. | .. | .. | 43·6        | 42·7   |
| Paraffin   | .. | .. | .. | .. | .. | .. | 35·1        | 34·7   |

I have analysed since a number of samples of soaps, and always obtained the rosin distinctly brittle, and therefore practically free from fat. This I found to be the case even when the percentage of rosin was so low as 4 or 5 per cent.

In my experiments the caustic soda solution was normal, but a more dilute solution might be used with advantage, as a smaller sample could be taken, and the operation considerably hastened.

The figures given have been those actually obtained, without correction for error, such as unsaponifiable matter in the original rosin, which would affect the gravimetric determination. The volumetric method I would prefer in all cases, except where an examination of the rosin was desired.

O. H.

### ANALYSIS OF SPIRITS.

THE following methods of examining spirits are taken from a paper handed in by Dr. James Bell, to the Select Committee (1891) on British and Foreign Spirits, and published as an appendix to their Report :—

*Estimation of the Free Acids in Spirits.*—50 c.c. of the spirit at proof strength are introduced into a glass retort and distilled to dryness by the aid of a gentle heat. The distillate is exactly neutralised with pure decinormal hydrate of barium, phenol



phthalein solution being used throughout to indicate when the neutral point is reached. The solution of the barium salt is then evaporated to dryness in a platinum capsule, and the weight of dry salt ascertained. The salt is afterwards dissolved in water without removing it from the capsule, and decinormal sulphuric acid is added in quantity slightly greater than the  $\frac{N}{10}$  barium previously used, whereby the whole of the barium is converted into barium sulphate. This is brought to dryness and afterwards ignited for a few seconds, whereby the slight excess of sulphuric acid is expelled and pure sulphate of barium only left in the capsule. The weight of sulphate of barium is then ascertained, and from this and the amount of barium salt of the organic acids previously obtained, the actual and the molecular weights of the mixed acids are determined by calculation.

*Estimation of the Compound Ethers in Spirits.*—50 c.c. of the spirit at proof strength, if nearly colourless, is directly neutralised with  $\frac{N}{10}$  barium solution; but if much coloured the spirit is first distilled, as in the case of the estimation of the free acids, before neutralising. The exactly neutral spirit is placed in a glass retort and distilled to dryness. The first portion of the distillate measuring 30 c.c., is collected separately from the last fraction of rather more than 20 c.c. The distillates are placed in two strong assay flasks, and an exact quantity of decinormal barium solution added to the extent of 3 or 4 c.c., greater than experience had shown to be necessary to decompose all the ethers. The flasks are then secured with indiarubber corks tied down with leather or canvas, and kept at a temperature of nearly  $212^{\circ}$  F. for three hours. The separation of the distillates into two parts affords a useful qualitative test as to the character of the compound ethers present. When the ethers consist chiefly of acetic ether, about  $\frac{1}{10}$  only of the whole will be found in the second fraction; but where the higher combined acids, especially those of the vegetable fats, are present in more than average quantity, the proportion of compound ether in the last fraction will equal  $\frac{1}{3}$  or  $\frac{1}{2}$  of the total ethers. After saponification is complete and the contents of the flasks cooled, decinormal sulphuric acid is run in until the excess of barium has been neutralised. The quantity of barium solution originally used, therefore, less the quantity left after saponification, expresses the amount of combined acids in the ethers in terms of decinormal strength. Taking acetic ether as the basis for calculation we obtain .0088 gramme of acetic ether for every c.c. of  $\frac{N}{10}$  barium used in the saponification; from which the total weight of ether present is calculated according to the actual proportion of barium solution used in the decomposition of the ether. To obtain the molecular and actual weights of the mixed acids, the residues in the flasks, after being neutralised with sulphuric acid, are mixed and evaporated to one-third, the sulphate of barium filtered, and the filtrate which now contains only barium salts of the organic acids, is evaporated to dryness, and the weight ascertained. The salt is treated exactly as in the case of that obtained from the "free acids," the results affording data from which the molecular and actual weights of the combined acids can be ascertained.

To determine the quantity of each acid it is necessary to operate upon from 200 c.c. to 500 c.c., according to the amount of compound ethers present. The barium salt is obtained in the manner above stated, its weight determined, and after being dissolved in water is placed in a suitable retort and distilled with successive quantities of  $\frac{N}{10}$   $\text{SO}_3$ , say

from 8 c.c. to 12 c.c., according to the quantity of individual acids judged to be present. The several fractions are kept distinct, neutralised with barium solution, evaporated to dryness, and the weight and combining equivalent of the acids determined, as detailed under "free acids."

To determine the difficult problem as to what extent the higher alcohols exist as alcohol radicles in the compound ethers, the furfural reaction has been utilised. When pure alcohol is mixed with, say,  $\frac{1}{10}$  of one per cent. of a compound ether containing the radicle of amyl alcohol, the characteristic purple colour is not produced when furfural and concentrated sulphuric acid are added thereto. But if the ether be decomposed and the amyl alcohol set free the furfural reaction is then obtained. The results obtained from the application of this method show that the higher alcohols exist as radicles in the compound only in minute proportion.

*Estimation of the Higher Alcohols in Spirits.*—100 c.c. of the spirit at proof strength are digested with a sufficiency of barium hydrate to neutralise the free acids and decompose all the compound ethers present. The alcohol is then distilled completely from the barium salts, and diluted with distilled water to a specific gravity of  $\cdot 979 = 30$  per cent. of proof spirit. The diluted spirit is introduced into a glass separator with 35 c.c. of chloroform, and briskly shaken for two or three minutes. The chloroform is allowed to settle down, and is then drawn off. This operation is repeated twice with similar quantities of chloroform, and afterwards the three chloroform extracts are placed together in a separator and well shaken with an equal volume of distilled water, in order to free the chloroform from any ethylic alcohol. The washing process is performed three times. To the chloroform extract, now measuring over 100 c.c., are added from 15 to 30 c.c. of decinormal permanganate of potassium, according to the nature of the spirit tested, and 10 c.c. of normal sulphuric acid. The flask containing the mixture is secured with an india-rubber stopper tied down with canvas and kept in a cupboard, having a temperature about  $80^{\circ}$  F., for three days, the mixture being well shaken from time to time during that period. If it be observed that the permanganate is becoming nearly all de-oxidised, a further quantity of from 5 to 15 c.c. is added to the chloroform mixture. After oxidation is regarded as complete, a few drops of sulphurous acid are added to decolourise the unchanged permanganate, and a quantity of normal soda is added to produce a distinctly alkaline reaction. The whole is again returned to the separator, and strongly shaken up, so as to wash out from the chloroform any of the organic acids which may have passed into solution. The chloroform is run off, and again kept in contact for a day or two, with a few c.c.'s of permanganate solution and sulphuric acid, in order to prove whether complete oxidation of the alcohols has taken place or not. The alkaline solution of the organic acid is rendered slightly acid with sulphuric acid, and sulphate of silver added, until it ceases to produce a precipitate. The silver chloride and insoluble oxide of manganese are filtered off, and the colourless filtrate introduced into a suitable glass retort with 10 c.c. of normal sulphuric acid, and the organic acids completely distilled into a solution of pure decinormal barium hydrate. The solution of barium salt obtained and rendered perfectly neutral, is then evaporated to dryness in a platinum capsule, weighed, and subsequently estimated in the same way as the barium salt, from the free acids, and those obtained from the compound ethers. In estimating

the amount of the alcohols from the ascertained weight of the acids obtained from the oxidation of the higher alcohols, the factor  $\cdot 84$  is used as a multiplier, which is found in agreement with the average combining equivalent of the mixed higher acids.

**A New Method of Quantitative Analysis.** By A. BAUMANN (*Zeit. für angew. Chemie*, 1891, 135—142, 203—210, 328—332).—This method depends upon the reaction between chromic acid and hydrogen dioxide in presence of sulphuric acid, whereby oxygen is evolved. Lunge (*Chem. Ind.* 1885, 6) and Berthelot (*Compt. Rend.* 1889, 24, 157, 477) assert that this action is not quantitatively constant, but the author's experiments prove that one molecule of chromic acid evolves 4 atoms of oxygen, while one molecule of potassium dichromate evolves 8 atoms, when acted on by hydrogen dioxide in dilute solution and in presence of sulphuric acid.

A Wagner's azotometer (*Zeit. Anal. Chem.* 13), or that of Knop (*ibid.* 1886, 301) with a Wagner's evolution-flask adapted to it, is the best apparatus for the processes described in this abstract. The evolution-flask is an ordinary flask in which is sealed a small glass cylinder.

For the estimation of chromic acid the solution containing it, which may measure from 10.50 c.c., but should not be too concentrated, is placed in the outer chamber of the flask together with 10 c.c. of dilute sulphuric acid (1 : 5). Five to 10 c.c. of commercial hydrogen dioxide are then placed in the glass cylinder, or inner chamber of the flask, the apparatus is connected up, and allowed to stand in water at the temperature of the room for ten or fifteen minutes. The water in the U tube of the azotometer is now adjusted at zero and levelled, the stop-cock of the connecting tube closed, and the flask thoroughly shaken for five or six minutes, the cock being opened at the end of the first half minute and minute to allow most of the oxygen to pass into the measuring tube. When the volume of gas in the apparatus (which after shaking is, of course, replaced, with the stop-cock open, in the water), no longer increases, it is measured, reduced to zero and 760 mm., and the number of c.c. multiplied by 2.246 to obtain the quantity of chromic acid present, for 1 c.c. of oxygen = 2.246 mgms.  $\text{CrO}_3$ .

Hydrochloric acid (1 : 2) can be substituted for sulphuric acid in the above process, and nitric acid may be present to the extent of not more than 0.2 gramme. Acetic and succinic acids do not interfere, but, of course, all substances which are oxidisable by chromic acid must be absent.

The titration of standard potassium dichromate solution is rapidly and accurately effected by this method, for the available oxygen of the solution is three-eighths of the total oxygen evolved.

Chromic oxide is estimated by first oxidising it with hydrogen dioxide in alkaline solution, then strongly boiling to destroy the excess of the hydrogen dioxide, neutralising with sulphuric acid, and proceeding to estimate the chromic acid as above. 1 c.c. of oxygen at  $0^\circ$  and 760 mm. = 1.710 mgms.  $\text{Cr}_2\text{O}_3$ .

To estimate sulphuric acid by this method, the solution, which must not contain a large excess of hydrochloric acid and only a very little nitric acid or nitrates, is put into

a 100 c.c. flask, and precipitated in the cold with a solution of barium chromate in hydrochloric acid. After the flask has been well shaken and allowed to rest for half an hour, 90 c.c. of water are added and ammonia until the liquid is alkaline. The flask is filled to the mark, shaken, and the liquid filtered through a dry double filter; 25-60 c.c. of the filtrate are transferred to the evolution-flask, 10 c.c. of sulphuric acid are added, and the estimation conducted as already described for chromic acid. One c.c. of oxygen at  $0^{\circ}$  and 760 mm. = 1.787636 mgms.  $\text{SO}_3$ . The "purest" barium chromate must be thoroughly washed to free it from potassium or ammonium chromate before use; it is then boiled while still moist with hydrochloric acid (3 per cent.), and filtered from the undissolved residue, the filtrate being ready for use. Tables are given in the original showing the results of the estimation of sulphuric acid and the quantity of  $\text{SO}_3$  corresponding to 1 c.c. of oxygen measured under various conditions of temperature and pressure.

*Estimation of Lead*.—Sodium acetate is first added to the liquid to substitute acetic acid for any free nitric or other acid which may be present, or may be liberated on the addition of dichromate; the solution is heated to boiling, and potassium dichromate solution added by degrees until the liquid becomes pale yellow, a large excess being avoided. The lead chromate thus precipitated is filtered and washed with water; the filter is spread out on a glass plate, and the precipitate spurted with dilute sulphuric acid into the outer chamber of the evolution flask. Five to 6 c.c. of hydrogen dioxide (2 per cent.) are then placed in the glass cylinder, the apparatus connected up, and the process completed as already described. One c.c. of oxygen at  $0^{\circ}$  and 760 mm. = 4.9776 mgms.  $\text{PbO}$ . ( $\text{Pb} = 206.4$ ).

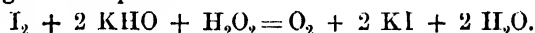
If the quantity of lead chromate be large (say 200 mgms.) it must be digested for some hours with the dilute sulphuric acid before the hydrogen dioxide is mixed with it, to ensure the liberation of all the chromic acid; moreover, some 15 to 20 minutes' shaking will be necessary before all the oxygen is liberated. When many analyses have to be performed, it is better to adopt the following indirect method:—The solution, which must be only very slightly acid with nitric acid, is diluted to about 50 c.c., placed in 100 c.c. flask, about 1 gramme of sodium acetate added, and the lead precipitated in the hot with a measured quantity of potassium dichromate, whose titre has been determined (see above), care being taken that the liquid is yellow. The mixture is then cooled, made up to 100 c.c., and filtered through a dry filter; 30-50 c.c. of the filtrate are mixed with 10 c.c. of dilute sulphuric acid, and the amount of chromic acid that has not combined with the lead determined as above.

*Estimation of Bismuth*.—The solution should only contain a very small quantity of free nitric acid; it is poured into a warm solution of a slight excess of potassium dichromate. The precipitate should be orange yellow throughout, and so dense that the red-yellow liquid rapidly becomes clear. If the precipitate be more the colour of egg-yolk, more dichromate must be added. The mixture is now heated for some ten minutes, the precipitate filtered and washed by heating and decantation with hot water, and dissolved in a little dilute hydrochloric acid; this solution is transferred to the outer chamber of the evolution-flask, 10 c.c. of dilute sulphuric acid (1:5) are added, and the determination completed as already described. One c.c. of oxygen at

0° and 760 mm. = 5.192 mgms. of bismuth oxide. The estimation may also be made indirectly as in the case of lead.

*Estimation of Barium.*—Barium cannot be completely precipitated as chromate by potassium dichromate even in the presence of sodium acetate, and if potassium chromate is used, the precipitate always contains some of the precipitant. Ammonium chromate is free from these objections. The solution containing the barium is heated, and a solution of ammonium chromate added until the liquid is yellow; the precipitate is filtered and washed, first with dilute ammonium chromate solution, finally with very dilute ammonia. The traces of precipitate which still cling to the beaker are dissolved in dilute hydrochloric acid, and the whole precipitate spurted with warm (60°) dilute hydrochloric acid (1 : 20) into the outer chamber of the evolution-flask; 10 c.c. of dilute sulphuric acid are added, and the estimation completed as already described. One c.c. of oxygen at 0° and 760 mm. = 3.42 mgms. of barium oxide. The indirect method may also be adopted, ammonium chromate being employed.

The author has also studied the action of iodine and its oxygen acids on hydrogen dioxide, and has founded some methods of analysis thereon. Iodine has only a "catalytic" action on hydrogen dioxide, evolving oxygen apparently without being itself affected; hence this reaction cannot be employed. A solution of iodine in potash, when acted on by hydrogen dioxide, evolves two atoms of oxygen for every two atoms of iodine with formation of potassium iodide. This reaction confirms the opinion which Schönbein put forward, that a solution of iodine in potash is really a solution of potassium hypoiodite, analogous to a solution of chlorine in potash, and not potassium iodate, as has been generally supposed; for a solution of potassium iodate evolves no oxygen from hydrogen dioxide; nor does a solution of potassium chlorate, whereas it is notorious that calcium hypochlorite can be accurately estimated by this method. The hypoiodite rapidly changes into iodate so that the hydrogen dioxide must be mixed with the solution as quickly as possible to obtain exact results; this is best attained by adding the neutral iodine solution to alkaline hydrogen dioxide. The text books have it that the iodine is first converted into iodate by the hydrogen dioxide, and that this then reacts on the dioxide; what has been said above shows that this is not the case, and as a fact the reaction takes place according to the equation:



To estimate free iodine and thus obtain the titre of a solution of iodine in potassium iodide, 40—50 c.c. of the solution are placed in the outer chamber of the flask, and 5 c.c. of hydrogen dioxide (5 per cent.) in the glass cylinder together with a solution of potassium hydroxide (1 part) in water (2 parts). When the apparatus has been cooled and adjusted, the evolution-flask is violently shaken, when nearly all the oxygen will be evolved in the first second, and the reaction will be complete in a minute; five minutes' cooling will therefore suffice before the volume of oxygen is read off. One c.c. of oxygen at 0° and 760 mm. = 11.33 mgms. of iodine ( $I = 126.54$ ). The applicability of this method to all iodometric processes will at once be appreciated; it is fully dwelt upon in the original paper. As a means of acidimetry it is very rapid, it being possible to determine free mineral acids in three minutes as follows:—1—2 grammes of finely-powdered potassium iodate, and 10 grammes of potassium iodide are

dissolved in a little water in the outer chamber of the evolution-flask, a measured quantity of the acid is added, and an equivalent of iodine having been liberated according to the well-known reaction of hydriodic acid on iodic acid, the whole is diluted to some 40 c.c. Hydrogen dioxide and potash are placed in the glass cylinder, and the estimation completed as described above. If organic acids (oxalic, tartaric, or acetic) are to be estimated they must be heated with the mixed iodide and iodate for half an hour at 70° c.c. before the equivalent of iodine will be liberated; with this precaution it becomes possible to estimate the acidity of beer and wine by this method.

The author deems it convenient to calculate the titre of an iodine solution in terms of hydrogen, and gives a table showing the weight in mgms. of 1 c.c. of hydrogen at temperatures from 10° to 25°, and at pressures from 700 to 770 mm. A. G. B.

**Examination of China Teas.** By P. DVORKOVITCH (*Journ. of Anal. and Applied Chem.*, Vol. v., p. 315).—The author estimates the amount of theine as follows:—10 grammes of tea are carefully ground and 200 c.c. boiling water are poured over it. Five minutes later the infusion is decanted. This operation is repeated three times. The tea is then boiled twice with 200 c.c. water each time so that the water is not coloured, or but slightly so. The extract thus obtained, is diluted to one litre. A portion of this extract is washed with petroleum ether three times, in order to remove the oil and the brown substance found in tea, to which Mulder has already called attention. Then 600 c.c. of this aqueous infusion, corresponding to 6 grammes tea, are taken, washed with petroleum ether, 100 c.c. of a caustic baryta solution, containing 4 grammes in 100 c.c. are added to it, well shaken and filtered immediately from the precipitate obtained. 583 grammes of the filtrate, corresponding to 5 grammes of tea, are then mixed with 100 c.c. of twenty per cent. salt solution and the mixture shaken with chloroform three times, about 400 grammes chloroform being used in all. The solvent is then removed by distillation, and the residue of theine dried at 100° C. Absolutely white theine is obtained in beautiful needle-shaped crystals.

The washing with petroleum ether is necessary, first, for the removal of the ethereal oil, and next, for that of the brown substance alluded to. One and the same tea, washed and not washed with petroleum ether, showed a difference of 0.6 p.c. in its contents of theine. This method gives higher results than that of Peligot, Mulder, or J. Bell. All methods based on Mulder's principle, viz., on the boiling of the tea with magnesia or lime, give results which are too low, on account of the partial destruction of the theine with evolution of ammonia.

The preliminary fermentation, to which all black teas are subjected, destroys a varying proportion of the tannin. The quality of the tea, to a very great extent, depends upon the method of fermentation, the astringency not only being lessened thereby, but the aroma being developed. The author worked out a method applicable to the determination of the tannin and to its products of fermentation, based upon the Loewenthal principle. A solution of tea, 10 grammes to the litre, is made, precisely as above described, 40 c.c. being diluted with 500 c.c. of water, and titrated with permanganate,

with indigo carmine as indicator. 80 c.c. of the tea solution are then mixed with 20 c.c. of caustic baryta containing 4 grammes. In 100 c.c. the precipitate is filtered off and 50 c.c. titrated with permanganate. The quantity of permanganate thus expended indicates the quantity of the products of the decomposition of tannin; that is to say, the degree of fermentation to which the leaf was subjected. The longer the fermentation lasted, the more of these products. The percentage both of tannin and the products of fermentation are calculated from the oxalic acid standard of the permanganate solution, 63 grammes of oxalic acid corresponding, according to the author, to 31.3 grammes of tannin, and not to 41.2, as found by Neubauer.

Twenty-nine samples of tea were examined. The best qualities contained the largest amounts of theine. This was manifested more strongly when the ratio of theine to the total amount of tannin and products of fermentation was calculated. The theine varied from 2.14 in the cheapest, to 3.21 in the best tea; the percentage of theine to total tannin from 16.0 to 24.52.

It need hardly be added that these deductions are in direct contradiction with those of many other observers.

O. H.

**The Saponification of Esters by Sodium Ethylate.** A. Kossel and M. Kruger. (*Zeits. Physiol. Chem.* 1891, 321, *through Chem. Zeit.*).—The authors have examined the action of sodium ethylate in the cold upon esters containing fatty acids. The decomposition is similar to that produced by ordinary means of saponification, the final products being the sodium salts of the fatty acids and the alcohol with which they were combined. For example, cetyl palmitate prepared from spermaceti, when dissolved in ether and subjected to the action of sodium ethylate in the cold, yields cetyl alcohol on extraction of the products of the reaction with ether, while sodium palmitate remains.

A corresponding decomposition is effected on treating phenyl salicylate (salol) with sodium ethylate, save that besides salicylic acid and phenol, ethyl salicylate is formed. On substituting sodium amylate for the ethylate, the products include amyl salicylate.

With regard to the application of the method for the saponification of fats, the authors recommend treating 5 grammes of the fat dissolved in ether with a quantity of sodium ethylate, containing 0.5 to 0.7 gramme of sodium. Although the saponification proceeds in the cold on shaking, yet it can be hastened by heating on the water-bath and evaporating off the solvent, the whole operation being effected in 12–20 minutes, according to the quantity of liquid present. The solution of sodium ethylate must be made fresh each time. 5 grammes of clean sodium are dissolved in 100 c.c. of absolute alcohol under a vertical condenser, without special effort to control the reaction by cooling. 10 c.c. of this solution suffice for 5 grammes of tallow, and 15 c.c. for the same quantity of butter-fat. In determining the insoluble fatty acids by the Hühner process, 5 grammes of the fat are weighed into a 250 c.c. flask, covered with 10–20 c.c. of absolute alcohol, warmed in the water-bath, and 10–15 c.c. of the solution of sodium ethylate added. Saponification is quickly effected, the alcohol

is driven off by heating the flask on a water-bath briskly boiling, and the dry soap heated for some time in the same way. It is then dissolved in 100 c.c. of water, and the process carried out as usual. The results are the same as when alcoholic potash is used.

B. B.

**Weighing Bottle for Oils.** R. Hefelmann. (*Chem. Zeit.* 15, 1891, 989).—The device consists of a weighing bottle shaped liked an Erlenmeyer flask, into the neck of which is ground a 2 c.c. pipette, marked at 0.1, 0.2, and 0.5 c.c. (for quantities of oil suitable for the determination of the iodine number), and at 1, 1.5, and 2 c.c. (for such purposes as the determination of the saponification equivalent). The upper end of the pipette is closed by a little rubber cap (such as is used for the “fillers” of reservoir pens), by means of which the oil can be drawn up into the pipette to the required height. The pipette may be fitted to the mouth of the weighing bottle by means of a cork instead of by being ground in, but in this case the cork must be constantly renewed lest it should contaminate the oil being examined with traces of a previous sample, a portion of which may have been absorbed by it.

B. B.

**Technical Analysis of Charcoal from the Dregs of Beetroot Molasses.** C. Heyer. (*Chem. Zeit.* 15, 1891, 915, and 959—960).—The ordinary method of determining the total potash, and that present as potassium chloride in this charcoal, consists in estimating the potassium as potassio-platinic chloride after conversion of the sulphates into chlorides by the addition of the exact quantity of barium chloride found to be necessary in a previous determination of the sulphates, and in titrating the chlorides of another portion after neutralisation with nitric acid by means of standard, silver solution. Samples that had been well ignited, and were almost free from nitrogen, gave accurate results when thus treated, whereas those that had been imperfectly burnt, as well as some that appeared fairly well burnt, were found to contain appreciable quantities of nitrogen, and to yield erroneous figures. It must be also mentioned that the nitrogen is not wholly present as ammonium salts, part being in the form of cyanogen compounds; ammonia is evolved slowly on boiling with water or potash lye, and even on prolonged heating does not correspond to the total nitrogen present, as determined by the Kjeldahl process.

If the analysis be conducted directly on the aqueous extract of the charcoal, three errors therefore occur:—

- (1). The ammonium is reckoned as potassium.
- (2). The cyanides are reckoned as chlorides.
- (3). The sulphur of sulphides and thiocyanates is not determined, and the former salts are reckoned as carbonates.

The first error is avoided by evaporating the aqueous extract to dryness, and igniting the residue, thus driving off the ammonium salts. The second is prevented by heating the solution neutralised with nitric acid previous to titrating the chlorine, so as to get rid of hydrocyanic acid. The third difficulty is overcome partly by the ignition



and partly by oxidising any remaining sulphur compounds to sulphates by treatment with nitric acid or bromine water before precipitating with barium chloride.

Analyses showing large discrepancies due to the neglect of these precautions are appended to the paper. B. B.

**Vessels for Containing Hydrofluoric Acid.** R. BENEDIKT (*Chem. Zeit.*, 15, 1891, 881).—The guttapercha bottles generally used for containing hydrofluoric acid always yield a certain amount of soluble matter, which leaves a considerable residue (chiefly consisting of ferric oxide) on evaporation and ignition. Although platinum is undoubtedly the best material for the purpose, the author has found hard rubber (vulcanite) to be an efficient substitute; a sample of acid that had been kept in a bottle of this material for more than a year only yielding a residue of 0.0005 gramme from 25 c.c. Hydrofluosilicic acid can be kept in such bottles equally well. B. B.

**Determination of Manganese in Iron and Steel.** H. RUBRICIUS (*Chem. Zeit.*, 15, 1891, 882).—Contrary to sundry assertions that have been made, that the end point in titrating manganese with permanganate solution is difficult to see, the author finds that it can readily be discerned, and recommends the following process:—

10 grammes of iron or steel are dissolved in 50 c.c. of hydrochloric acid of sp. gr. 1.15; the solution diluted filtered into a 500 c.c. flask, made up to the mark and 100 c.c. of the liquid (= 2 grammes of the original substance) oxidised with nitric acid, cooled, diluted to 600-700 c.c., nearly neutralised with sodium carbonate, the iron precipitated with zinc oxide, 2-3 grammes of magnesium sulphate added, the solution brought to the boiling point and titrated with permanganate. Thorough oxidation and the use of only a moderate excess of zinc oxide are conditions essential to success. The process takes one and a half to two hours to carry out. On account of the dilution being considerable, a slight excess of permanganate (about 0.1 c.c. of  $\frac{N}{10}$  solution) is necessary to produce a definite pink colouration. The test analyses given are satisfactory. B. B.

## CORRESPONDENCE.

*To the Sub-Editor of the ANALYST.*

SIR,—In performing the turmeric test for the detection of borax and boracic acid in milk, I prefer to evaporate one or two drops of the suspected sample with an equal quantity of tincture turmeric, and then add a drop of oil HCl (drawing the acid over the residue with a glass rod), apply heat again for a few seconds, when, if either of the substances tested for are present, a colour ranging from a pink to a dark red will be produced. Remove the capsule immediately, and confirm the presence of borates with a drop of ammonia. The test seems to be more delicate when performed in this manner, as it avoids the blackening of the residue which may occur when strong HCl is added to the milk and tincture turmeric previous to evaporation.—Very truly yours,

JAMES O. JORDAN,

Office of the Inspector of Milk, Butter, and Vinegar,  
Boston, Aug. 3rd, 1891.

Chemist to the Milk Department.

**ERRATA.**—In the August number, page 158, third line from foot, not counting foot-note, opposite the words "Insoluble matter (Ignited)," for 0.44 read 0.15; second line from foot, for 100.06 read 99.77. Page 160, line 23, for Ed. Maanbdl Vervalsch, read Dr. P. E. van Hamel Roos (*Revue Internat. d. Falsifications*, 1891, p. 166–167).

# THE ANALYST.

OCTOBER, 1891.

## ANALYSIS OF SUGAR, MOLASSES, AND SYRUP.

BY F. W. BABINGTON, F.I.C., ASSISTANT ANALYST, INLAND REVENUE LABORATORY,  
OTTAWA.

HAVING a number of sugars and syrups to test, and rapidity of work being desirable, I have modified some existing processes to suit my case. As my principal object was the detection of starch syrup, the analysis of the whole of the samples had to be completed as soon as possible, so as to sort them out. The process I used is as follows:—

The reagents, etc., employed, were the following:— 1. Animal charcoal in fine powder after twelve hours digestion in dilute hydrochloric acid, washing and re-ignition. 2. Alumina cream, prepared by precipitating a solution of alum with ammonia, washing thoroughly, and allowing the precipitate to consolidate to a cream. 3. Fehling solution which consisted of a mixture of solutions A and B in equal volumes; A contained 34.639 grammes of pure copper sulphate dissolved in water, filtered and made up to 500 cubic centimetres; B contained 173 grammes Rochelle salt dissolved in 300 c.c. water, with 40 grammes sodium hydrate added, dissolved and made up to 500 c.c., and then filtered through glass wool or asbestos fibre. 4. A nearly saturated solution of carbonate of soda. 5. The asbestos filters used for obtaining and weighing the cuprous oxide were constructed in the following manner: A “Macfarlane milk tube” is used for containing the filtering materials. Such tubes are specially made for this laboratory, but may be made from a 50 c.c. pipette with long bulb, by cutting the latter across in the middle, and leaving enough of the small tubes at the other ends to pass through a perforated cork. A piece of platinum gauze or perforated platinum foil is placed at the bottom of the wide part of the tube, sufficiently large to prevent the asbestos from being drawn through, and the tube is inserted in the perforation of a rubber stopper, closing a Bunsen filtering flask, which is connected with an exhausting apparatus. The latter is put in operation, and a loose layer of common asbestos fibre (crysotile), about an inch deep, placed upon the platinum gauze. A thin pulp made of Italian or hornblende asbestos is then poured into the tube in sufficient quantity to form a filtering bed. This pulp is made by scraping down a piece of hornblende asbestos in the direction of the fibre, digesting it for one hour with 4 per cent. soda solution, and washing thoroughly. Sufficient pulp must be poured into the tube to form a layer one-eighth to one-fourth of an inch in thickness. The filter is then washed once with alcohol and once with ether, dried thoroughly in the water-bath, cooled in the dessicator, and weighed. With regard to the details of the processes used, the following may be mentioned:—

*Saccharimeter Readings.*—The saccharimeter employed is manufactured by Schmidt and Haensch, Berlin, and is known as the Soleil-Ventzke-Scheibler apparatus, the reading giving the percentage of cane sugar direct. 13.024 grammes of the sugar are taken and dissolved and washed, by means of 50 or 60 c.c. warm water, into a flask of 100 c.c. capacity; 1 gramme animal charcoal is added, and agitated occasionally for half an hour; then 20 to 30 c.c. alumina cream is introduced into the flask, mixed with its contents, cooled and made up to the 100 c.c. mark. The solution is then filtered through a dry ribbed filter into a dry flask, introduced into the 200 millimetre tube, and read in the saccharimeter. The reading  $\times 2$  gives the percentage. Syrups and molasses are treated in the same way as the sugars, but sometimes require more animal charcoal or have to be read in the 100 m.m. tube.

*Clerget Inversion.*—50 c.c. of the same solution prepared for the saccharimeter reading are placed in a 50 c.c. flask provided with a mark at 55 c.c.; 2.5 c.c. of strong hydrochloric acid are added and mixed with the solution. The flask is then immersed in water, the temperature of the latter raised to  $70^{\circ}\text{C}$ ., and kept between  $60^{\circ}$  and  $70^{\circ}$  for twenty minutes. The flask is next cooled to room temperature, made up to 55 c.c., and the solution placed in a 200 m.m. tube fitted with a thermometer and observed in the saccharimeter. The temperature of the solution can also be determined in the ordinary tube immediately after its removal from the saccharimeter. The reading should be (unless in the case of samples containing dextrose or starch syrup) to the left (or -), and its amount, which in the case of sugars varies from -13 to -14 at  $20^{\circ}\text{C}$ ., should be increased one-tenth, on account of the dilution. The Clerget formula is then applied, viz. :—

$$\frac{(\text{Direct reading} + \text{invert reading}) \times 200}{142.7 - \frac{1}{2} \text{ temp. of invert.}} = \text{percentage of cane sugar.}$$

*Reducing Sugars.*—In the case of samples of white or yellow sugar,  $2\frac{1}{2}$  grammes are taken, dissolved and washed in a 50 c.c. flask by the use of about 25 c.c. warm water. 50 c.c. of undiluted Fehling solution are placed in a small beaker, and the latter, as well as the 50 c.c. flask, are immersed in boiling water, and allowed to remain until their contents have about the same temperature as the surrounding water. The sugar solution is then poured into the beaker, and the flask washed out with hot water, not more than about 25 c.c. being used, so that the resulting mixture may not exceed 100 c.c. in bulk. The beaker is allowed to remain in the boiling water for exactly ten minutes longer, and then the solution containing the precipitated cuprous oxide is poured into the weighed asbestos filter, standing in connection with the exhausting apparatus. If the filter has been properly made the filtration proceeds as rapidly as the liquid can be poured in, and the precipitate can be very rapidly washed into it with hot water. The filter is then filled up three or four times with hot water, and, when the filtrate gives no alkaline reaction with litmus paper, the tube is filled up once with alcohol and a second time with ether. While this is going on, it is convenient to proceed with the precipitation of another assay, which has been previously heated up in the boiling water. After the washing with ether, the

tube is heated in a steam bath, to complete dryness (about two hours is usually sufficient), cooled in the desiccator, and weighed. The increase in weight of the tube multiplied by 0.4861 and 40 gives the percentage of reducing sugars.

*Cane Sugar by Inversion and Fehling's Solution.*— In testing white and yellow sugars, 0.25 gramme is washed into a 50 c.c. flask by using 25 to 30 c.c. of warm water ; 0.5 c.c. of strong hydrochloric acid is added and the mixture inverted by heating, as in the Clerget inversion process. It is then neutralised by solution of soda carbonate, the quantity necessary having been previously ascertained in a blank experiment. Excess of the soda carbonate must be avoided, as it interferes with the correctness of the result. The precipitation, filtration and washing are conducted as described above, under reducing sugars, but 60 c.c. of Fehling solution are used instead of 50, and the bulk of the mixture made up to 110 instead of 100 c.c.m. The increase of weight which the tube experiences,  $\times 0.4861$ ,  $\times 400$  gives the percentage of invert sugar resulting from the cane sugar. This, minus the percentage of reducing sugar  $\times 0.95$ , gives the percentage of cane sugar.

With syrups and molasses 5 grammes of the sample are washed into a 250 c.c. flask and made up to the mark ; 25 c.c. are used for the reducing sugars, and the same quantity is inverted for the cane sugar. Precipitation, filtration and washing are conducted in the same way as in the case of the yellow and white sugars, excepting that 60 c.c. Fehling's solution are used in determining the reducing sugars and 70 to 80 c.c. of the Fehling when the cane sugar is to be estimated, and that, further, 2 c.c. of the strong hydrochloric acid are used for the inversion, and a corresponding quantity of soda carbonate for neutralising it.

*Moisture and Water.*—The moisture in the white and yellow sugars was determined by drying 2 grammes to constant weight. In the case of the syrups and molasses, the quantity of water was ascertained by dissolving 20 grammes in warm water, and diluting to 100 c.c. and introducing 20 c.c. of this solution ( $\therefore$  4 grammes of the sample) into ordinary asbestos fibre (crysotile) contained in a milk tube, the tube and contents having been previously dried and weighed. The milk tubes used in this case had an inside diameter of 40 m.m., a depth of about 35 m.m., with an opening at bottom 5 m.m. in diameter, into a small tube 8 m.m. in length. The tube, with contents, is placed in a water-bath and dried at from  $90^{\circ}$  to  $100^{\circ}$  C. The drying is complete in 48 hours, and the increased weight of the tube and contents gives the amount of dry substance contained in 4 grammes of the sample, water found by difference.

As regards the rapidity of this process, six samples can be completely finished in duplicate, with the exception of the moisture, in eight hours, and by taking aliquot parts of the solution prepared for the polariscope reading for the precipitation, the weighing would be avoided and the work expedited ; but I have preferred to make a separate weighing, as a more complete check.

As regards the accuracy, that depends, of course, on the manipulation, and probably the factor obtained may vary for the same reason, but if the same method is adhered to, the results obtained will be at all events comparable. The following table gives the data of some work done for that purpose.

|  | Number of determinations. | Direct polariscope in per cent. | Invert polariscope in per cent. | By Clergel. | Direct.       |                                 |                           |         | Inverted.     |                                 |                           |         | Cane sugar by difference of $\text{Cu}_2\text{O}$ . | Other sugars by difference of $\text{Cu}_2\text{O}$ . | Water. |
|--|---------------------------|---------------------------------|---------------------------------|-------------|---------------|---------------------------------|---------------------------|---------|---------------|---------------------------------|---------------------------|---------|---|---|--------|
|  |                           |                                 |                                 |             | Amount taken. | $\text{Cu}_2\text{O}$ obtained. | Difference, max. and min. | Factor. | Amount taken. | $\text{Cu}_2\text{O}$ obtained. | Difference, max. and min. | Factor. |   |   |        |
| Cane sugar ..  | 10                        | + 100                           | ..                              | ..          | .25           | .001                            | .0005                     | ..      | .25           | .541                            | .002                      | .4861   | 99.92   | ..  | .0     |
| Grape sugar (corn) ..  | 4                         | + 79.6                          | + 79.7                          | ..          | .25           | .530                            | .002                      | .4717   | 25            | .5385                           | .001                      | ..      | ..  | 100.00  | .0     |
| Equal weights grape<br>and cane sugars   | 4                         | + 88.92                         | + 25.84                         | 49.40       | .50           | .532                            | .003                      | .4717   | .25           | .547                            | .004                      | ..      | 50.35   | 50.18   | .0     |
| Milk sugar ..  | 4                         | + 76.8                          | + 78.6                          | ..          | .25           | .361                            | .001                      | .6944   | .25           | .363                            | .004                      | ..      | ..  | 100.26  | .0     |
| Starch syrup ..  | 4                         | + 153.8                         | + 151.0                         | ..          | .5            | .463                            | .004                      | 1.08    | .5            | .477                            | .044                      | ..      | ..  | ..  | ..     |
| 50 pts. starch syrup<br>50 " cane syrup<br>50 " water<br>33.3 per cent. of each. | 4                         | + 43.1                          | + 21.0                          | 34.3        | .5            | .166                            | .002                      | 1.08    | .5            | .536                            | .002                      | ..      | 34.6  | 35.86   | ..     |

In addition to the foregoing particulars regarding methods of examination and manipulation, I may state that the constant for the Clerget inversion, 142.7, is taken from the redeterminations by Wohl, given in "Spencer's Handbook for Sugar Manufacturers" (p. 116). The half normal weight for the quantity of sugar was taken because, with the saccharimeter used, accurate readings to the left were not obtainable with the normal weight. It must also be mentioned that the factor, 0.4861, used for calculating the amount of reducing sugars from the cuprous oxide, was ascertained from a number of determinations of the quantity of the oxide yielded by pure cane sugar after inversion. These determinations agreed closely, but it is quite possible that changes in the manipulations by other operators would alter the factor. Basic lead acetate was not used for clarifying in any of the above analysis, in order to avoid the lead error, or the trouble of removing the lead previous to inversion.

Some of the syrup and molasses samples show greater differences than usual between the results obtained by direct and inverted saccharimeter reading. The differences reappeared even when basic lead acetate was employed to clarify, and were probably due to the presence of unusually large amounts of syrup-forming substances different from sugar. All these analyses were done in duplicate, but I do not consider this to be necessary, as the optical and chemical results check each other and are equivalent to a duplicate analysis.

In giving these details regarding the processes used, it is not intended to suggest that these should be substituted for others now in use. But since, in the examination of saccharine substances, many different methods of analysis are in use, the results of which may vary slightly according to the nature of the process and the mode of manipulation, I have thought it necessary to give these particulars, in order that they may be taken into consideration when comparisons are being made with the results above stated and the work of other analysts.

#### SUGGESTIONS FOR THE ASSAY OF ACONITE AND ITS PREPARATIONS.\*

By ALFRED H. ALLEN, F.I.C., F.C.S.

THE importance attaching to the assay and standardising of preparations of aconite is universally admitted, but the exceptional difficulties connected with the problem have hitherto prevented any satisfactory solution.

The extraction of the total alkaloids from aconite-root can be effected with tolerable ease, and by the use of judiciously chosen methods the bases can be isolated fairly pure, and without having undergone any material change; but the determination of the total alkaloids of an aconite preparation is, in itself, of limited value as a criterion of its activity. It is rather the first step in the process of assay, the potency of the preparation substantially depending on the results subsequently obtained.

Where the amount of material is insufficient, there is no doubt that it is very desirable to isolate the crystallisable alkaloid, and if this could be effected with an

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\* Abstract of a paper read before the British Pharmaceutical Conference at Cardiff.

approach to quantitative accuracy, it would probably furnish the most reliable criterion of the physiological activity of the substance. In practice, however, the amount of substance which is commonly available, or can be conveniently submitted to examination, yields a quantity of total alkaloids far too small to render any method based on crystallisation practically available.

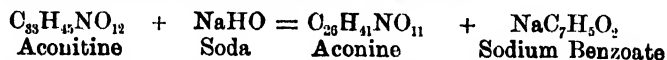
Under these circumstances, I have, with the assistance of Mr. G. E. Scott Smith, recently made some experiments to ascertain how far a method based on the saponification of the crystallisable alkaloids could be applied to the very small quantities of material isolated in an ordinary assay. That the saponification occurs with a near approach to quantitative accuracy was clearly established by Dr. C. R. Alder Wright, who also proposed to apply the reaction to the actual assay of aconite alkaloids. Hence, I have thought it unnecessary to repeat Wright's classical experiments, and have sought rather to adapt his researches to the particular object in question, namely, the examination of very small quantities of aconite alkaloids.

The following table represents the composition of the three principal saponifiable alkaloids of aconite, and shows the products of their saponification :—

| Crystallisable alkaloid.                         |                         | Products of Saponification. |                |        |                |                |                       |
|--|-------------------------|-----------------------------|----------------|--------|----------------|----------------|-----------------------|
|  |                         | Acid product.               |                |        |                | Basic product. |                       |
| Name.  | Formula.                | Name.                       | Formula.       | Yield. | NaHO required. | Nature.        | Formula.              |
| Aconitine<br>(from <i>A. Napellus</i> )          | $C_{33}H_{45}NO_{12}$   | Benzoic acid                | $C_7H_6O_2$    | 18.92  | 6.20           | Aconine        | $C_{26}H_{41}NO_{11}$ |
| Japaconitine<br>(from <i>A. Fischeri</i> , etc.) | $C_{60}H_{88}N_2O_{21}$ | Benzoic acid                | $C_7H_6O_2$    | 19.60  | 6.43           | Japaconine     | $C_{53}H_{81}NO_{10}$ |
| Pseudaconitine<br>(from <i>A. Ferox</i> )        | $C_{36}H_{40}NO_{12}$   | Veratric acid               | $C_9H_{10}O_4$ | 26.49  | 5.82           | Pseudaconine   | $C_{27}H_{41}NO_9$    |

A method of assay, based on the saponification of the crystallisable alkaloids, has the great merit of distinguishing sharply between the three principal poisonous aconite bases on the one hand, and the comparatively inactive products of their decomposition on the other. In fact, as it is generally accepted that aconine has only  $\frac{1}{300}$  of the physiological activity of aconitine, and that japaconine and pseudaconine bear a similar relation to their respective parent alkaloids, it may be safely assumed that the activity of a mixture of aconite alkaloids is substantially represented by the proportion of saponifiable base present, and, therefore, if the latter can be ascertained with an approach to quantitative accuracy, a considerable advance will have been made towards the solution of the problem of the assay of aconite preparations.

The reaction of aconitine with caustic soda is as follows :—



The saponification of japaconitine and pseudaconitine may be expressed by similar

equations, bearing in mind that the former alkaloid reacts with  $2\text{NaHO}$  with the formation of two molecules of sodium benzoate and two of japaconine.

Wright's saponification experiments were made on comparatively large quantities of alkaloids; but to be of practical value the method of assay must be available with a quantity of aconite bases not exceeding 50 milligrammes, and should even be applicable with half that quantity, or less than  $\frac{1}{10}$  of a grain. I may fairly claim to have achieved a certain amount of success in dealing with these small quantities, a success which is in great measure due to the use of two reagents, methyl-orange and phenolphthalein, neither of which had come into use at the period of Wright's researches. Methyl-orange is sensitive only to the strongest acids, but reacts with the weakest bases. Hence all the ordinary alkaloids may be treated with accuracy by its aid. Phenolphthalein, on the other hand, is sensitive to the weakest acids, but is quite unacted on by the majority of the alkaloids; atropine, homatropine, and hyoscyamine being the most notable exceptions. Sulphate of quinine, hydrochloride of morphine, and hydrochloride of aniline are perfectly neutral to methyl-orange, but react with phenolphthalein just as if the acids were in a free state.\* As phenolphthalein is sensitive to carbonic acid, no sharp results can be obtained unless the standard alkali used in titrating be quite free from carbonate. This is insured by employing baryta-water as the standard alkaline solution, and experience has convinced me that this reagent is at least twice as sensitive as the most carefully prepared caustic soda. Either hydrochloric or sulphuric acid is suitable as the standard acid; oxalic acid does not react well with methyl-orange. As very minute quantities of acid and alkali are in question, it is necessary to employ very dilute standard solutions. The water used for diluting them must be recently boiled and rigidly neutral in reaction. The standard solutions we have adopted are of  $\frac{1}{50}$  normal strength. Where the alkaloids of aconite have been isolated and obtained in a fairly pure condition, they may be determined with great facility by titration with standard acid in the following manner:—

A weight of 30 milligrammes of pure crystallised alkaloid, or about twice that quantity of the mixed alkaloids from aconite, is dissolved in about 15 c.c. of (neutral) ether, and the solution placed in a small stoppered cylinder, together with 3 c.c. of water containing a drop of a  $\frac{1}{10}$  per cent. solution of methyl-orange and previously rendered sensibly pink by a minute addition of acid.

Standard hydrochloric or sulphuric acid of  $\frac{1}{50}$  normal strength ( $\frac{36.5}{50}$  of  $\text{HCl}$ , or  $\frac{49}{50}$  grammes of  $\text{H}_2\text{SO}_4$  per litre) is then carefully added from an accurately divided burette or pipette, with vigorous agitation between each addition. The addition of acid is continued until the lower aqueous layer retains a red tint after thorough agitation with the ethereal layer. Operating in this manner the reaction is extremely delicate, for the brownish colour exhibited by the ethereal layer, when an impure alkaloid is titrated, in no way interferes, but presents a marked contrast to the colour of the aqueous liquid.

|   |       |                           |
|---|-------|---------------------------|
| 1 c.c. of $\frac{1}{50}$ acid neutralises | 12.94 | milligrammes of aconitine |
| " "                                       | 10.86 | " aconine                 |
| " "                                       | 14.14 | " pseudaconitine          |
| " "                                       | 10.46 | " pseudaconine            |
| " "                                       | 12.44 | " japaconitine            |
| " "                                       | 10.54 | " japaconine              |

\* Morphine does not give a sharp end-reaction with phenolphthalein



Operating on crystallised aconitine, two experiments made in this manner showed 29.9 and 31.0 milligrammes of alkaloid against 30.0 taken, while 30.0 milligrammes of japaconitine (not quite pure) showed 29.8 by titration.

The neutralised solution obtained in the foregoing titration may be conveniently employed for estimating the proportion of saponifiable alkaloid in the following manner, but the process is equally applicable to an ordinary chloroform or ether residue. The residue or solution, containing from 30 to 80 grammes of alkaloid, is treated with 20 c.c. of rectified spirit (neutral to phenolphthalein), and 3 c.c. of a solution of caustic soda in an equal weight of water. The liquid is then boiled for an hour in a flask under a reflux condenser, after which the alcohol is distilled off and the residual liquid acidulated with hydrochloric acid. The liberated benzoic or veratric acid is extracted by agitation with about 15 c.c. of ether, and the ethereal solution separated and washed with successive small quantities of water, until the washings show their freedom from mineral acid by ceasing to redden litmus. The ethereal liquid is then separated and transferred to a small stoppered cylinder (25 c.c. capacity), about 5 c.c. of water faintly coloured with phenolphthalein added, and  $\frac{1}{50}$  normal baryta water dropped in from a finely-divided pipette, until the aqueous layer acquires a pink colour, which is not destroyed by agitation with the ethereal stratum. From the volume of standard baryta consumed, the amount of aromatic acid resulting from the saponification can be calculated. 1 c.c. of  $\frac{N}{50}$  baryta neutralises 2.44 grammes of benzoic or 3.64 grammes of veratric (dimethyl protocatechuic) acid. Although these acids have different combining weights, the volumes of alkali neutralised by equivalent weights of them are of course identical, and hence no grave difference results in calculating the saponifiable alkaloids, whether benzoic or veratric acid has been produced by the saponification. Thus:—

|  |   |
|--|---|
| 1 c.c. of $\frac{N}{10}$ baryta represents | 12.94 milligrammes of aconitine saponified. |
| " "  | 14.14 " pseudoaconitine.                    |
| " "  | 12.14 " japaconitine.                       |

In three experiments, where a weight of 30 milligrammes of the same sample of crystallised aconitine was saponified, the baryta solution used represented 31.6, 28.3, and 30.9 of the alkaloid. In the case of japaconitine (not quite pure) the process indicated 21.8 against 30 milligrammes taken.

If desired, the titration being completed, hydrochloric acid may be added, when the aromatic acid will be liberated and re-dissolved by the ether. On separating this solution, and allowing it to evaporate spontaneously, the weight of the acid may be ascertained and its melting point observed; or the ether may be separated from the aqueous liquid, and the latter acidulated, largely diluted and distilled, when a separation of the benzoic and veratric acids will be effected, the former volatilising with the steam and the latter remaining in the retort. This difference of behaviour enables pseudoaconitine to be recognised and estimated in presence of aconitine and japaconitine.

By the foregoing method of assaying the mixed alkaloids from tincture of *Aconitum Napellus* root,\* Mr. G. E. Scott-Smith obtained in my laboratory the following results:—

\* The alkaloids from a tincture prepared from the root of *A. Ferrox* gave, for 7.67 mgrms taken, by titration 74.9 of alkaloid, calculated as pseudoaconitine; saponified, 14.3 mgrms of veratric acid by titration, against a weight of 13.0 extracted by ether. The former result represents 55.1 of pseudoaconite, leaving 21.6 of unsaponifiable alkaloid. The basic product of the saponification, extracted by ether followed by chloroform from the alkaline residue, amounted to 18.5 milligrammes and neutralised acid equivalent to 51.4 of pseudoaconine, or 69.4 of pseudoaconitine.

|   | A.   | B.   | C.   | D.   | E.   | F.   | G.   | H.   |
|---|------|------|------|------|------|------|------|------|
| Weight taken in milligrammes .. ..            | 55.0 | 51.7 | 26.0 | 87.0 | 21.0 | 31.5 | 17.2 | 23.5 |
| Alkaloid by titration (in terms of aconitine) | 67.0 | 66.7 | 29.4 | —    | 28.8 | —    | 18.1 | 24.9 |
| Benzoic acid .. .. .                          | 5.2  | 4.0  | —    | 8.4  | —    | 4.8  | 4.1  |      |
| = Aconitine .. .. .                           | 27.7 | 20.4 | —    | 44.5 | —    | 25.7 | 22.1 |      |
| Percentage of saponifiable alkaloid ..        | 50.4 | 39.5 | —    | 51.1 | —    | 81.6 | 56.1 |      |

If desired, the basic product of the saponification can be isolated by rendering the liquid alkaline with sodium carbonate or caustic soda, and agitating with ether or chloroform. The latter solvent extracts a trifling further quantity from the liquid which has already been treated with ether. The few experiments we made in this direction gave somewhat erratic results.

The results of the saponification process appear to be somewhat uncertain so far as the basic products are concerned, probably in part owing to incomplete extraction, and in part because of the further change aconine is known to suffer when heated with caustic alkali. But as the proportion of saponifiable or active alkaloid is deduced from the acid product, and this can be determined with facility and great accuracy, the immediate object of the research may be said to have been effected.

How far japaconitine and pseudaconitine may be considered equivalent to aconitine in physiological activity I do not intend to discuss, but may say that the balance of evidence seems to show that the three alkaloids are approximately equally active when in a pure, crystallised, and unchanged state.\*

So far I have regarded aconitine, japaconitine, and pseudaconitine as practically the only alkaloids concerned in the physiological activity of preparations of aconite. But these three alkaloids are not the only saponifiable bases of the aconites. Thus *lyaconitine*, the amorphous alkaloid of *Aconitum lycoctonum*, also yields an acid and one or more bases on saponification (of which one, lycoctonine, readily crystallises), but it is doubtful if the reaction can be expressed by any simple formula. *Picraconitine* was isolated by Mr. T. B. Groves from a parcel, purchased in 1874, as roots of *Aconitum napellus*, of German growth. It is an amorphous, bitter, non-poisonous alkaloid, forming a crystallisable hydrochloride and nitrate, and was found by C. R. A. Wright to yield benzoic acid and a basic principle on saponification. Although *picraconitine* is well characterised, it does not appear ever to have been met with again, unless the imperfectly-examined bitter alkaloid obtained by E. L. Cleaver from the root of *Aconitum paniculatum* was identical therewith. At any rate, in the absence of further evidence of its presence, we may regard *picraconitine* as too rare a base to require consideration in devising a process for the assay of aconite. Besides, its unrecognised presence in a preparation would merely result in the saponification test indicating a greater proportion of physiologically active alkaloid than actually existed, so that the error would be on the right side.†

\* In the original paper the author gives reason for doubting whether the aconitine of commerce is of constant toxicity even when perfectly crystalline.

† The same argument applies to other saponifiable bases of low physiological activity, provided they are present in relatively small proportion to the active saponifiable alkaloids; but should further research show these little-known bodies to be present in relatively considerable proportion, the value of the saponification test will be reduced accordingly.

**The Analysis of Blacking.** J. PINETTE. (*Chem. Zeit.*, 15, 1891, 916).—Victor Hölbling has already given a method for the analysis of blacking (Cf. J.S.C.I., 1885, p. 235). The author has devised the following simplifications:—About 5 grammes of the blacking are weighed out by the method of double weighing into a separating burette having a capacity of 200 c.c.; about 100 c.c. of water are added, and the burette filled nearly to the top mark with a mixture of equal parts of ether and petroleum ether. After shaking and separation 25 c.c. of the ethereal solution are drawn off by a pipette, dropped slowly through a dry filter-paper into a weighing bottle, and the filtrate, together with the washings of the paper, evaporated to dryness, and the residue (fat) weighed. An aliquot portion of the lower aqueous solution is drawn off, filtered and titrated with  $\frac{N}{10}$  caustic soda, using phenolphthalein as an indicator, giving the free acid. The value thus obtained represents phosphoric acid free or as an acid phosphate, and not, as Hölbling asserts, free sulphuric acid. The resulting neutral solution is evaporated to dryness in a platinum dish (which need not be previously weighed), weighed, ignited, and weighed again, giving the invert sugar and extractive material.

Another portion of the aqueous solution is neutralised with the determined quantity of caustic soda solution, evaporated on the water bath until it no longer smells of ether filtered, made up to 25 c.c., and the invert sugar determined by Fehling's solution. The difference between this figure and that previously obtained gives the extractive matter,

By this method four of the constituents are determined on one weighed portion. Water and ash are determined on another portion. The carbon is determined by difference. The complete analysis of the ash can be carried out as in a phosphate analysis. The author has used with satisfaction Jones' modification of the Glaser method for the estimation of lime. Lately, blacking free from acid has been put upon the market. A bituminous shale has been substituted for bone black in its manufacture. A shale from Osnabrück for this purpose contained 21.52 per cent. of bituminous matter and combined water. The carbonization of the molasses is omitted, the raw materials of the blacking consisting solely of fat, molasses, and the shale in question. The origin of the molasses can be ascertained by means of the polarimeter. The cane sugar can either be determined directly by the polarimeter, or gravimetrically after inversion. A preservative is added to the acid-free blacking if it shows any tendency to become mouldy.

The following are analyses typical of the two classes:—

|                               |    |    |    | Acid,—per cent. | Acid-free,—per cent. |
|-------------------------------|----|----|----|-----------------|----------------------|
| Water                         | .. | .. | .. | 23.84           | 13.28                |
| Fat                           | .. | .. | .. | 5.53            | 3.48                 |
| Free acid                     | .. | .. | .. | 1.66            | —                    |
| Invert sugar                  | .. | .. | .. | 20.14           | —                    |
| Cane sugar                    | .. | .. | .. | —               | 23.35                |
| Extractive matter             | .. | .. | .. | 3.40            | 10.81                |
| Carbon                        | .. | .. | .. | 7.86            | } 9.49               |
| Combined water                | .. | .. | .. | —               |                      |
| P <sub>2</sub> O <sub>5</sub> | .. | .. | .. | 10.24           | —                    |
| SO <sub>3</sub>               | .. | .. | .. | 8.76            | —                    |
| CaO                           | .. | .. | .. | 12.96           | —                    |
| Na <sub>2</sub> O             | .. | .. | .. | 5.61            | —                    |
| by † Clay (ignited)           | .. | .. | .. | —               | 39.59                |
|                               |    |    |    | 100.00          | 100.00               |

From these figures the percentages of the raw materials used may be reckoned, and are in round numbers :—

|   |    |    | Acid,—per cent. | Acid-free,—per cent. |
|---|----|----|-----------------|----------------------|
| Bone black .. ..                          | .. | .. | 13.0            | —                    |
| Molasses .. ..                            | .. | .. | 68.0            | 63.5                 |
| Sulphuric acid .. ..                      | .. | .. | 12.0            | —                    |
| Soda ash .. ..                            | .. | .. | 4.5             | —                    |
| Fat " .. ..                               | .. | .. | 2.5             | 2.5                  |
| Bituminous shale .. ..                    | .. | .. | —               | 31.0                 |
| (Containing 20 per cent. volatile matter) |    |    | 100.0           | 100.0                |

B. B.

**A New Reagent for Acetone.** A. SCHWICKER (*Chem. Zeit.*, 15, 1891, 914).—Powdered iodine acts upon a mixture of acetone and aqueous ammonia with the production of iodoform—a substance which is probably an iodine substitution product of acetone, and which has the property of exciting a flow of tears; acetic acid being formed simultaneously. Alcohol gives no reaction under these conditions and acetone can therefore be detected in its presence. The process is carried out as follows :—

To the solution to be tested are added a few drops of strong ammonia and one or two drops of iodine solution of about decinormal strength. Iodide of nitrogen at first forms, but disappears on shaking and warming. Unless the acetone be present in very small quantity a yellow turbidity of iodoform makes its appearance at this point, and is increased by the addition of one or two more drops of iodine solution. The characteristic smell of iodoform is also perceptible in spite of the ammonia. If the precipitate of iodide of nitrogen fail to disappear readily, it can be removed by treatment with a few drops of dilute sodium hyposulphite solution. When the solution of acetone is very dilute, more time should be given for the reaction before removing the iodide of nitrogen; the iodine solution should also be dilute. One part of acetone in 5,000 parts of solution can be detected by this means. The reaction can be used for the recognition of acetone in urine. Acetadehyde also gives the reaction.

B. B.

**The Röse Process for Determining Alcohol.** L. GRUNHUT (*Chem. Zeit.*, 15, 1891, 847, 848).—Röse's process, which was published about three years ago, consists in oxidising the alcohol with potassium permanganate, adding oxalic acid in excess and titrating back with permanganate. The alcohol is said to be completely oxidised to CO<sub>2</sub>. The author has found, as Benedikt did previously, that the reaction does not proceed regularly on these lines. Working with a distillate of which the alcoholic content had been determined by Hehner's tables, he found that, following Röse's prescription, only about half the quantity of permanganate, corresponding to the equation given by him, was used. The use of sulphuric acid in small quantity caused the reaction to take place nearly in accordance with the assumption that the alcohol was oxidised to acetic acid. When the proportion of sulphuric acid was increased, the oxidation was

more nearly complete, but the addition of large quantities of acid induces an independent decomposition of the permanganate and thus cannot be pushed to an extreme point.

It is possible that the spirit used being a crude product of fermentation, the reaction took place in a manner different from that observed by Ruse, who used pure spirit, but in any case, whether that be so or not, the method is inapplicable for the technical examination of ordinary alcohol.

B. B.

**The Determination of Bitartrate in Argols** (by the method of B. Phillips and Co.) B. Bailli. (*Chem. Zeit.* 15, 1891. 989 - 991.)—The principle of the method consists in converting the bitartrate into tartrate by treatment with potash or soda, and thus rendering it soluble, filtering its solution from the insoluble portion of the argol, precipitating the bitartrate by addition of acetic acid, and titration of the precipitate in the usual way.

G. Kämmer has introduced a modification, the difference of which lies in the fact that the neutralisation is performed cold instead of hot. With both methods the impurities present in crude tartar are found to interfere. If the tartar has been derived from plastered wine, the calcium sulphate present reacts, upon neutralisation, with a portion of the tartrate, precipitating it as calcium tartrate. It is true the potassium tartrate present tends to keep the calcium salt in solution; but the latter is deposited on dilution and standing. The evil can be mitigated by taking as little calcium sulphate into solution as possible. To this end the argol is extracted with a little *hot* water, avoiding stirring and boiling, and neutralizing the extract quickly. Unfortunately, these conditions are favourable to the maximum action of the insoluble carbonates that may also be present; besides this drawback, any advantage that might accrue from the use of this precaution is nullified by the necessity of diluting the aqueous extract to a known volume, which dilution brings about decomposition, as intimated above.

It is, therefore, better not to attempt to prevent the reaction taking place, but to ascertain how far it has gone by determining the amount of potassium sulphate in an aliquot portion of the tartrate solution. The portion taken must be evaporated to dryness and ignited, as precipitation of barium sulphate would be interfered with by the tartrates and other salts present in the solution before this treatment.

Even with all possible precautions, the author considers that Kämmer's method of analysis cannot be used for tartars from plastered wines.

The action of calcium carbonate which is a constant constituent of crude tartar upon bitartrate of potash, occurs in accordance with the following equation:—

$2\text{KHC}_4\text{H}_4\text{O}_6 + \text{CaCO}_3 = \text{H}_2\text{O} + \text{CO}_2 + \text{K}_2\text{C}_4\text{H}_4\text{O}_6 + \text{CaC}_2\text{H}_4\text{O}_6$ . Favourable conditions are concentration of the solution, heating and stirring. On the other hand, by neutralizing quickly and keeping, as suggested by Warrington, the alkaline liquid in excess from the first, the decomposition can be almost entirely arrested, as the neutral tartrate of potash is not attacked by calcium carbonate. The author, however, considers this precaution of limited utility, on the ground that the conditions are not those occurring

in practice, and the main object of tartrate analysis is to ascertain not the real contents of the material, but the quantity it may be expected to yield when treated on the large scale. The potassium carbonate, which is a frequent decomposition product of the bitartrate, and is therefore present in crude tartars, reacts with a portion of the bitartrate to form neutral tartrate. This is all reckoned as bitartrate in Kämmer's method of analysis, although valueless to the manufacturer. A correction may be applied by determining first the total tartrate, then the neutral tartrate, and deducting the one result from the other, and thus obtaining the real value for the bitartrate.

The following modified form of Kämmer's process is suggested. Until the exact behaviour of calcium sulphate in tartars from plastered wines is known, it is inapplicable to such materials. The analysis divides itself into two parts:—

I. *The Real or Main Analysis.*—The object of this is to determine the total tartrate extractible by water. 10 grammes of the finely powdered sample are boiled with 100 c.c. of water for 10 minutes. The hot solution is made neutral or slightly alkaline by the addition of caustic soda or potash. After cooling, the solution is made up to 200 c.c., filtered through a dry filter, and 40 c.c. of the filtrate evaporated to about 5 c.c. after the addition of about 2 grammes of potassium chloride, and 2–3 c.c. of glacial acetic acid and 100 c.c. of alcohol (90–95 per cent.) added with vigorous stirring. After allowing the precipitate to stand for a quarter to half an hour, it is filtered off, washed with alcohol, and titrated with semi-normal alkali. An aqueous solution of potassium chloride, saturated with bitartrate, may be used to wash with instead of alcohol, its tendency to decompose on keeping being done away with by the addition of 0.5–1.0 gramme of phenol per litre, thus allowing a large quantity to be prepared at one time.

The result of the titration is corrected for the volume of the insoluble residue by deducting the following quantity ( $0.6 - 0.005 \times$  per cent. of bitartrate found)  $\frac{1}{20}$ , which it will be seen varies with the richness of the sample. This correction is not rigidly accurate, as it assumes that the only matter going into solution is bitartrate; but the error is compensated for by its recurrence in the correction analysis about to be described.

II. *Correction Analysis.*—Two methods are available. The first or indirect method is the shorter but more operose; the other or direct method is simpler, but slower.

A. *Indirect Method.*—10 grammes of the sample are boiled for ten minutes with 100 c.c. of water made up to 200 c.c. and filtered; filtration is slow, and the filtrate somewhat turbid. As the filtrate contains some bitartrate as well as tartrate, one portion is used for the determination of their joint amount, and another for the bitartrate only. The former estimation is effected by adding 1 gramme of potassium chloride to 40 c.c. of the filtered solution, evaporating to about 10 c.c., adding 2–3 c.c. of glacial acetic acid, stirring vigorously for two minutes, and filtering after half an hour to one hour, washing off with alcohol the solution of potassium chloride previously mentioned. The precipitate is titrated, and the result corrected as before. The latter is carried out thus:—40 c.c. of the filtrate is treated with 1 gramme of potassium chloride evaporated to 10 c.c., cooled and stirred for two minutes. After half an hour to one hour the precipitate is filtered off, washed and titrated as usual. Direct titration of the 40 c.c. of solution taken gives incorrect results; the addition of alcohol must be avoided, as it precipitates a certain

amount of slimy matter. Also, as the only point necessary to be determined is the percentage of neutral tartrate—that is, the difference between the sum of the tartrate and bitartrate and the bitartrate itself—it is not essential to obtain complete precipitation in either case, provided precipitation be effected equally in each. On this account an alternative scheme consisting in precipitating in the 40 c.c. of solution taken with out previous concentration and allowing the precipitate to stand over-night, may be adopted.

It must here be noted that when the crude tartar has suffered decomposition to such an extent that its aqueous extract does not contain any bitartrate (a fact which may be ascertained by its behaviour on neutralization in the main analysis, and by the non-formation of crystals of bitartrate in the cooled solution about to be used for the correction analysis), the determination of the bitartrate alone, described above, is obviously needless; in this case, however, complete precipitation of the whole of the tartrate in solution must be attained by the ordinary means.

The importance of the correction thus obtained is shown by figures given in the original, the percentage of bitartrate corresponding to the neutral tartrate, for which allowance has to be made, ranging from 1.4 to 12.5 per cent. according to the character of the raw material.

B. *Direct Method*.—Seeing that the aqueous extract from the tartar may be viewed simply as a solution of neutral tartrate in a menstruum already saturated with bitartrate, it is plain that the addition of acetic acid by converting the neutral into bitartrate will precipitate an amount of the latter equivalent to that of the neutral tartrate, the percentage of which it is sought to determine. The method is inapplicable when the sample is decomposed and is only feeble acid or even alkaline in reaction, and during its execution no considerable variations of temperature must occur. Regard being had to these limitations, it is carried out as follows:—10 grammes of the sample are boiled with 100 c.c. of water for ten minutes, the solution diluted to 200 c.c., 2–3 grammes of pure potassium bitartrate added (always provided that some bitartrate be already present) and violently shaken so as to saturate the liquid with bitartrate. 40 c.c. of the filtered solution are precipitated with 2–3 c.c. of glacial acetic acid, without previous concentration, and allowed to stand over-night. Any important lowering of the temperature that may have taken place will be indicated by the deposition of bitartrate from another portion of the filtered solution which has not been acidified. The determination is completed as usual, and the correction for the volume of the insoluble portion made as before. The results agree with those given by the indirect method. B. B.

**A New Thermometric Scale.** F. Salomon. (*Zeitsch. f. Angew. Chem.* 1891, p. 409).—The author proposes a scale which has a relation to absolute zero, so that its readings directly indicate the volumes of gases at various temperatures. The starting point is  $-273^{\circ}$  C.; from this to the freezing point of water, the scale is divided into 100 equal parts, so that  $0^{\circ}$  C. corresponds to 100 of the new scale. From this to  $273^{\circ}$  C. the scale is again divided into 100 equal parts,  $273^{\circ}$  C. being 200, the same propor-

tion of division being continued as far as desired. Each degree of the scale is therefore equal to  $2.73^{\circ}$  C., and  $1^{\circ}$  C. to 0.3665 of the new scale; the boiling point of water lies at 136.6.

The use of the new scale is seen from the following examples:—One cubic metre of a gas at  $0^{\circ}$  C. or  $100^{\circ}$  absolute temperature would measure at the boiling point of water (136.6) 1366 litres. At  $200^{\circ}$  C. or  $173.2$  absolute temperature, it would have a volume of 1732 litres.

G. Lunge recommends this scale as forming the solution of a little difficulty which is felt in gas analysis.

O. H.

**On Tin in Preserved Articles of Food.** Van Hamel Roos. (*Revue Internationale des Falsifications*, Vol. 4, p. 179).—In the author's opinion, attention has not been sufficiently directed to the presence of tin in canned goods, and to the injurious effects traceable to the same. He reviews the work of previous writers on the subject, namely, Unger and Bodlaender, Sachs, Menche, and Hehner. Sedgwick (*Archives de Pharmacie*, 1888) was the first to prove poisonous effects in the case of some pears which had been prepared in a tinned saucepan, whilst another case is mentioned of chronic metallic poisoning from the use of tinned articles of food, terminating fatally.

Professor Beckurts communicated to the congress of German physicians, held at Heidelberg, in September, 1889, new observations of the presence of tin in canned goods, and called attention to the formation of tin sulphide, by the action of the albuminous matters upon tin, whilst Nehring, at the same congress, gave the amount of tin found in preserved asparagus as 0.186, 0.315, and 0.227 per cent. The result of the discussion was a recommendation by vote of the congress that tin plate should be forbidden for the making of vessels in which articles of food are to be preserved. Captain Winkel reported to the Hygienic Congress, held in Amsterdam, in September, 1890, that 270 soldiers had fallen ill after having eaten lettuce and meat, both preserved in tins; the amount of tin being, according to Professor Wefers Bettink, in Utrecht, from 19 to 72 milligrammes per kilo. Kayser, of Nuremberg, drew attention (*Revue Intern. des Falsif.*, Vol. 4, p. 29,) to the presence of 0.19 per cent. of tin in preserved eels, which had proved injurious to several persons eating the same.

The amount of tin dissolved depends greatly upon the length of time during which the article of food is in contact with the metal. Thus from a tin of asparagus, thirty-one years old, the tin had almost completely been dissolved off the iron; a tin of beef, eight years old, containing 970 grammes of beef, was contaminated with 77 milligrammes of oxide of tin; six year old asparagus 56 milligrammes; four months old asparagus only 11 milligrammes. Another tin of the same vegetable two years old, weighing 635 grammes, contained 36 milligrammes of oxide of tin, and 6 milligrammes oxide of copper. Apricots contained 20 milligrammes per tin, and pine apple 178 milligrammes per kilo.

Many other articles were examined, vegetable and animal, and all were found to contain more or less tin. Van Hamel Roos recommends that all tin, which are to be used for the packing of articles of food should have an interior coating of a special kind



of varnish. He finds that in tins thus protected, the amount of metal dissolved is inappreciable, but his experience extends only over about nine months. Sorrel, packed in a protected tin, quickly detached the varnish, and the tin was dissolved.

*Note by the abstractor.* Varnished tins have been used for very many years past by French manufacturers. This varnish is apt to contain lead, and the protection afforded by it is in any case but very partial, the solder of the lid not being coated.

O. H.

**The Concentration of Solutions as Estimated by their Refractive Power.** H. O. G. Ellinger. (*Jour. für. Prakt. Chem.* [2] 44, 152—157).—The apparatus employed is practically an Amagat-Jean oleorefractometer, but the author prefers to call it a “difference refractometer.” It consists of a collimator and a telescope with a common axis, between them is a cell with parallel glass sides containing another glass cell, the sides of which are inclined to one another like a prism; a trough surrounds both these cells, so that their temperature may be raised by immersion in warm water, although in his experiments the author allowed his liquids to remain at the temperature of the room. The collimator has a slide with a sharp vertical edge instead of a slit; this slide is moved by a millimetre screw. In the field of the telescope there is a transparent scale, which can be moved to the right or left by a fine adjustment and has 40 divisions engraved on the left, and 60 divisions on the right of the zero. All the cells have draw-off tubes provided with stopcocks.

The two inner cells are first filled with distilled water and the rays from the flame of a stearine candle are passed through the collimator. The field of the telescope is thus divided into light and dark with a sharp boundary line; if this line be coloured, or insufficiently defined, the light must be made monochromatic by the interposition of a piece of red glass between the source of the light and the collimator. The scale in the field is now moved until the zero coincides with the boundary line, and the water in the prism is replaced by the solution to be tested, a change which at once moves the boundary line in the field either to the right or to the left (according to the position of the prism) to an extent proportional to the strength of the solution. For example, a solution of sodium chloride containing 1 part per thousand shifts the boundary line 0.75 on the scale; a solution containing 1 per cent. shifts it 7.5, 2 per cent. shifts it 15, 5 per cent. shifts it 38.

By calibrating the instrument with solutions of various salts of known strengths it is possible to calculate the “parts per thousand factor,” that is the number by which the deflection must be multiplied in order to find the parts per thousand of the salt present in a solution of unknown strength. A solution which gives a high deflection must be diluted, or the accuracy of the method will be impaired; the determinations can be made very rapidly.

The author gives a table of “parts per thousand factors” for various salts, sugar, dextrin and gum; it is not reproduced here because it probably only applies to his own instrument. Examples of the accuracy of the method both for salts and for dilute alcohol are also given.

A. G. B.

**The Optical Analysis of Butter-fat.** By H. O. G. Ellinger. (*Jour. für Prakt. Chem.* [2] 44, 157—159).—The author has tested 510 samples of pure Danish butter in the Amagat-Jean oleorefractometer (see last Abstract) with a view to ascertaining how far the refraction of pure butter varies, a fact which it is very necessary to know before attempting to use the instrument for detecting admixture of fats other than butter in commercial butter. The Amagat-Jean "normal oil" was used in the outer of the two glass cells, and the trough was kept at a temperature of 45°.

The butter samples were taken at different seasons as follows:—

|                                |    |    |    |    |     |         |
|--------------------------------|----|----|----|----|-----|---------|
| A. February to June, inclusive | .. | .. | .. | .. | 209 | samples |
| B. September and October       | .. | .. | .. | .. | 174 | "       |
| C. November                    | .. | .. | .. | .. | 57  | "       |
| D. December                    | .. | .. | .. | .. | 70  | "       |

The readings are tabulated below; the first column shows the deflection and the others the number of samples in each season which gave that deflection:—

|      | A. | B. | C. | D. |      | A. | B. | C. | D. |      | A. | B. | C. | D. |
|------|----|----|----|----|------|----|----|----|----|------|----|----|----|----|
| 37   | 1  | —  | —  | —  | 31·5 | 16 | 8  | 1  | 2  | 27   | 3  | 21 | 1  | —  |
| 36   | 1  | —  | —  | —  | 31   | 33 | 14 | 3  | 1  | 26·5 | —  | 9  | 2  | —  |
| 35   | 1  | —  | 4  | 5  | 30·5 | 12 | 5  | 1  | 1  | 26   | —  | 22 | 2  | —  |
| 34·5 | 1  | —  | —  | —  | 30   | 32 | 7  | 2  | 1  | 25·5 | —  | 4  | 1  | —  |
| 34   | 6  | 1  | 10 | 11 | 29·5 | 9  | 5  | —  | —  | 25   | —  | 31 | 3  | —  |
| 33·5 | 2  | —  | 1  | 8  | 29   | 18 | 3  | —  | —  | 24·5 | —  | 8  | —  | —  |
| 33   | 13 | 2  | 8  | 22 | 28·5 | 12 | —  | 1  | —  | 24   | —  | 8  | 1  | —  |
| 32·5 | 6  | 1  | —  | 6  | 28   | 16 | 10 | 4  | —  | 23·5 | —  | 1  | 2  | —  |
| 32   | 26 | 7  | 8  | 14 | 27·5 | 1  | 4  | 1  | —  | 23   | —  | 3  | 1  | —  |

Mean deflection of A 30·5, B 27, C 30·5, D 33. The samples giving 37° and 36° were so abnormal in other respects that the author rejects them, and regards the variation of deflection caused by natural butter as 35°—23°.

The various sorts of margarine have a somewhat varied admixture of butter-fat, and, therefore, varied refractive indices. The sample which contained least butter (about  $\frac{1}{2}$  per cent.) was found to give a deflection of 8°. If natural butter giving the highest reading (35°) is mixed with an equal quantity of such margarine, the reading obtained is 21·5°, that is, only 1·5° lower than the lowest reading for natural butter (23°). Thus the method only shows the presence of more than 45 per cent. of margarine in such butter. Butter made during the first half and the latter part of the year can be mixed with as much as 30 per cent. of margarine without being condemned by the oleorefractometer.

A. G. B.

**Optical Estimation of Albumin in Urine.** By H. O. G. Ellinger. (*Journ. für. Prakt. Chem.* [2] 44, 256).—The difference refractometer (see last Abstract but one) may be employed for estimating albumin in urine as follows:—The prism and rectan-

gular cells are filled with the specimen of urine, the light of the stearine candle is passed through them, and the border line between the light and dark in the field of the telescope is made to coincide with the zero mark of the scale. The albumin is precipitated from another portion of the sample by means of heat and a drop of dilute acetic acid; it is filtered off, and the filtrate, made up to the original volume, is substituted for the sample in the rectangular cell, the prism cell remaining filled with the sample. The deflection of the border line now observed in the field of the telescope will be proportional to the quantity of albumin in the urine. With five different samples the author obtained the readings 2.5, 4, 4.5, 5, 5, respectively, while the parts of albumin per thousand, as found by the gravimetric method were 2.71, 4.36, 4.94, 5.10, 5.22, respectively. He, therefore, concludes that the method is sufficiently accurate for practice. A. G. B.

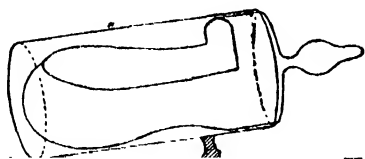
**A New Method of Separating Iron, Aluminium, and Chromium.** C. Marchal and J. Wlornik. (*Zeitsch. f. angew. Chem.*, 1891, p. 511).—Of the methods hitherto in use, the best are those of Woehler and of Gibbs. Woehler passes chlorine into the solution of the metals, previously rendered strongly alkaline with caustic alkali, until all chromium is oxidised into chromate. Gibbs renders the solution almost neutral with sodium carbonate, and then adds sodium acetate, oxidising with chlorine or bromine. Both these methods are useless in the presence of very small quantities of chromium.

The authors find that recently precipitated hydrated manganese peroxide oxidises chromium in neutral or nearly neutral solution into chromate, whilst all the iron is precipitated as ferric hydrate. The manganese peroxide is made by adding to a solution of permanganate an equivalent quantity of manganese sulphate and washing the precipitate. The solution of the metal, to be tested qualitatively, is heated for a few minutes with a small quantity of the peroxide, when the least trace of chromium reveals itself by the yellow colour of the solution. Thus chromium can be detected in samples of sulphate of alumina made from Irish bauxite, in which by the older methods no trace of chromium can be found.

For quantitative determinations the authors operate as follows:—The solution of the oxides in sulphuric or hydrochloric acid is neutralised with sodium carbonate until a small precipitate is produced. This is again re-dissolved in a drop or two of dilute acid; some precipitated manganese peroxide is added, and the mixture boiled for about ten minutes, to ascertain whether a sufficient quantity of peroxide has been added. A drop of the clear solution is tested with potassium ferrocyanide. If all iron is precipitated, the whole of the chromium is oxidised. The precipitate is then filtered off. The solution contains the whole of the alumina and the chromium, besides some manganese; the precipitate the whole of the iron as oxide, and manganese. From the filtrate the alumina is precipitated by ammonia, and carries down with it the manganese; these are separated by the usual basic precipitation method, while the precipitate containing the iron is dissolved in hydrochloric acid, the iron being also separated from the manganese by basic precipitation.

O. H.

**New Weighing-Bottle.** C. Mangold (*Zeitsch. f. angewandte Chem.*, 1891, page 441).--The ordinary form of weighing-bottle, with ground in stopper, has the disadvantage that when a finely-powdered substance is emptied out of it, a portion is liable to adhere to the ground portion of the neck, and upon re-insertion of the stopper to be driven out and lost. To remedy this, the author proposes a weighing-bottle of the form illustrated. The bottle has a little



foot, which supports it in an inclined position. The hollow scoop-like expansion of the stopper allows the removal of its contents to be effected without a chance of touching the ground portion of the bottle. The new form is very convenient for the determination of

hygroscopic moisture; the bottle and its contents are placed in the water-bath, and the stopper is slightly withdrawn. Since the substance is exposed in a thin layer, drying takes place with great rapidity.

W. J. S.

**On the Volumetric Estimation of Minute Quantities of Alkali.** F. Mylius and F. Förster. (*Ber. Deutsch. Chem. Gesellsch.*, 1891, p. 1,482.) The authors base their method on the extreme delicacy of iodeosin (erythrocosin) as an indicator, when used in an entirely novel manner. The commercial preparations of erythrocosin require purification before they can be applied to this purpose, since they contain small quantities of impurities (almost insoluble in ether), which communicate a blue-violet tint to alkaline solutions. For purification the commercial dye is dissolved in ether saturated with water, filtered, and the filtrate shaken up with dilute solution of caustic soda. The erythrocosin passes into the ether, and from this it is precipitated as a brick-red sodium salt by the further addition of caustic soda solution. The precipitate is filtered off, washed with spirit, and crystallised from hot alcohol, the impurities remaining behind in the mother liquor. For titration  $\frac{N}{1000}$  solutions are used, which must be made with pure or neutralised water. Water kept in vessels of inferior glass soon shows signs of impurity;  $\frac{N}{1000}$  solutions, however, if kept in vessels of good glass are stable for some time. The titration is performed in a stoppered flask, 50 to 100 c.c. of the aqueous fluid to be investigated are shaken with 10 to 20 c.c. of ether, containing in solution not more than 2 milligrammes of the purified erythrocosin per litre. Such a solution is almost colourless; but if free alkali be present, the aqueous layer, after shaking, appears of a rose-red colour. Upon neutralisation it again becomes colourless. The titration is best ended by adding alkali until a faint rose colour is produced 0.2 c.c. being deducted from the total quantity of alkali used. The influence of carbon dioxide on the result is practically *nil*, hence the carbonates in water may be easily and conveniently estimated by this process, the amount of acid used being the measure of the combined carbon dioxide. In like manner can be demonstrated the solubility of calcium carbonate in water; the decomposition which ensues on heating solutions of ammonium salts shown, the absolute neutrality of salts secured, etc. Examples are

given showing that salts, even when obtained from first-class houses, are seldom absolutely neutral. The neutrality of zinc salts, otherwise so difficult, is easily ascertained by this process. The oxides of magnesium, cadmium, manganese, nickel, and cobalt behave like zinc oxide; those of iron, aluminium, and chromium act as free acids. Since silver and platinum form insoluble compounds with the indicator, the testing of the salts of these metals is rendered difficult. The method is useless for the estimation of vegetable acids. For ascertaining smaller quantities than the equivalent of 0.1 mgrm. of sodium hydroxide, the authors propose a colorimetric modification of their process. This is, however, much too elaborate and complicated for ordinary practical work.

W. J. S.

**At what Degree of Acidity does Milk Curdle on Boiling?** W. Thorner. (*Chem. Zeit.* 15, 1891, 1108, 1109).—The author calls the number of tenths of a c.c. of  $\frac{N}{10}$  alkali required to neutralise the acid in 10 c.c. of milk (using phenolphthalein as an indicator), the "degree of acidity" of the sample.

He finds that milk as bought about 3—4 hours after milking has an acidity of  $12^{\circ}$ — $16^{\circ}$ , after a further period of 6 hours  $14^{\circ}$ — $25^{\circ}$ , after another 24 hours  $17^{\circ}$ — $60^{\circ}$ , and when 48 hours more have elapsed  $30^{\circ}$ — $100$ . The cooler the milk is kept the slower does the acidity increase. Light has little effect.

By experiments on milk kept under various conditions he found that it coagulates on boiling when it has an acidity of about  $23^{\circ}$ . Adopting  $20^{\circ}$  as the permissible limit he formulates the following simple test: 10 c.c. of the well-mixed sample is diluted to 30 c.c. with water, a few drops of phenolphthalein added, and 2 c.c. of  $\frac{N}{10}$  KOH solution run in. If a red colouration is produced, even though it be weak, the milk will not coagulate on boiling.

B. B.

**Copper in Preserved Foods.** J. Mayrhofer. (*Proc. Annual Meeting of the Freien Vereinigung Bayerischer Vertreter der Angewandten Chemie. Through Chem. Zeit.* 15, 1891, 1054.)—The copper occurring in various preserved articles of food is derived either from the vessels used in its preparation, or is purposely added. The juice of fruit preserved with sugar contained 4—9 mgrms of copper per kilo, the whole of this having come from the copper boilers, etc. In other cases where a green colour is derived the quantity ranges from 26—36 mgrms per kilo, and in one instance 76 mgrms were found. Part of this is intentionally added.

In the discussion which followed the reading of the paper, Barth stated that a green colour would be imparted to some vegetables, such as peas, by the use of vegetable colouring matters, while beans could not be thus treated effectively. Kochler mentioned that he had ascertained that the colour of some beautifully bright green beans, shown at the Strassburg exhibition, had been produced by passing a current of electricity through the copper vessel in which they were prepared, the vessel itself serving as the anode. The opinion of the meeting was divided as to the harmfulness of the practice.

B. B.

*Note.*—Extract of parsley has been used by trade preservers.—O. H.

# THE ANALYST.

NOVEMBER, 1891.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE opening meeting of the Session 1891-2 was held on Wednesday, the 7th ult., Dr. P. Vieth (in the absence of the President) being in the chair. The minutes of the last meeting having been read and confirmed, and Mr. Edgar B. Kenrick having been formally proposed as a member of the Society, Mr. A. H. Allen read the following paper:—

### FURTHER NOTES ON ACETIN.

BY A. H. ALLEN AND D. HOMFRAY.

IN a paper published in the September number of the ANALYST, we showed that when acetin was dissolved in alcohol together with a very small proportion of caustic alkali, the mixture gave, on distillation, a quantity of ethyl acetate which constituted a large proportion of the acetin employed, and which was largely in excess of the chemical equivalent of the caustic alkali used.

Since the publication of the paper containing an account of these researches, further experiments have shown us that a larger proportion of alkali diminished the yield of acetic ether. Thus, with sufficient caustic soda to saponify 12·7 per cent. of the acetin used, 85·2 per cent. of the acetic acid passed into the distillate as ethyl acetate. This, with the 12·7 remaining in the retort as sodium acetate, leaves only 2·1 per cent. unsaponified or otherwise to be accounted for. In another experiment in which the alkali used was equivalent to 39·8 per cent. of the acetin, the amount converted into acetic ether was 52·4 per cent., leaving 7·8 per cent. unaccounted for. In all cases the distillates were found to be neutral to phenolphthalein, showing that no free acetic acid had distilled over. The residues in the distilling flasks were always found to be slightly, but distinctly, *acid* to phenolphthalein, a fact which proves that the whole of the alkali employed invariably entered into reaction, and that some reaction occurs resulting in the production of free acetic acid. Hence it appears probable that the first action of the alkali on the acetin is to affect its hydrolysis, with the formation of glycerin and free acetic acid. A portion of the latter then reacts with the alkali to form sodium acetate, while the greater part reacts with the alcohol to form ethyl acetate; but a small proportion of the acetic

acid fails to enter into this latter reaction, and hence remains in the free state in the distilling flask. Why the soda should effect the hydrolysis of a much larger amount of acetin than it can chemically react with is not clear; but the behaviour of soda is evidently similar to that of lime, magnesia, and oxide of zinc, very small amounts of which (2 or 3 per cent.) are found to very greatly facilitate the hydrolysis of fats by super-heated steam, and are largely employed with this object.

A few supplementary experiments deserve mention. One gramme of anhydrous sodium acetate was distilled with 50 c.c. of alcohol, the distillate boiled with alkali and titrated back with standard acid, when it was found that no acetic ether had been formed. A mixture of acetin, alcohol, and anhydrous sodium acetate gave a small yield of acetic ether. It seemed possible that this result might be due to the presence of alkali in the sodium acetate. Hence the experiment was repeated by dissolving sodium acetate in alcohol, dropping in acetic acid till the alkaline reaction to phenolphthalein disappeared, and then adding acetin and distilling as before. Acetic ether, equivalent to 1.36 and 1.50 per cent. of the acetin taken, was found in the distillate. This is no more than was obtained by distilling acetin and alcohol together.

#### DISCUSSION.

The Chairman having invited discussion,

Mr. Bertram Blount wished to call attention to a phenomenon which seemed to him to be analogous to that described by the authors, namely, the fact that the complete saponification of a fat, and the determination of the saponification-equivalent was not possible unless a considerable excess of potash was used. If, for instance, one attempted to saponify cocoa-nut oil as in the Koettstorfer process, with only a slight excess of potash, the liquid might have a perfectly definite alkaline reaction to phenolphthalein, and use an appreciable quantity of acid on titrating back; nevertheless, when the experiment came to be figured out, it would be found to be entirely wrong, for the simple reason that saponification had never been completed.

The Chairman regarded the President's absence as being especially regrettable on this occasion, because he had done more work than any member present, with the exception of Mr. Allen, in connexion with the analysis of fats. Referring to Mr. Allen's remark that the reaction described by him was similar to that which took place in the decomposition of fats by superheated steam, and considering that the reaction now before them must take place at a rather low temperature, seeing that an alcoholic solution of potash was employed, it seemed to him that some further light might be thrown on the subject if the action were tried at higher temperatures with a view of ascertaining whether or not it was more energetic under such circumstances.

Mr. Allen, in reply, said that, dealing with the Chairman's remarks first, he would simply say that it was hardly possible that the reaction should be much more energetic under any circumstances, seeing that they already had about 85 per cent. of the original acetin converted into acetic ether. He was very much inclined to agree with

Mr. Blount's suggestion. Taking cocoa-nut oil as being laurate of glycy, one would expect the same reaction between that and alcoholic potash as occurred with the butyrate, acetate, stearate, and palmitate. The matter was of considerable interest, because it threw light on several phenomena, difficult to explain, yet frequently met with in practice; and further, because all the work in connection with it had arisen out of the investigation of the curious reaction between butter and alcoholic potash, described by Messrs. Wanklyn and Fox, which had excited considerable controversy, but which had been shown by him (Mr. Allen) to be only one of a large series of similar reactions.

The reading of Mr. T. P. Blunt's paper on Tabarie's Process for the Indirect Determination of Alcohol was unavoidably postponed until next meeting.

Mr. A. H. Allen then took the Chair, and Dr. P. Vieth read a paper on :—

#### FAT-EXTRACTION AND FAT-CALCULATION IN MILK ANALYSIS.

By DR. P. VIETH.

THE practical value of a mathematical formula expressing the relation between specific gravity, total solids, and fat in milk, is now very generally acknowledged by those analytical chemists who pay more than a superficial attention to milk analysis. The more frequently such a formula is proved to be in accordance with the actual facts, the more confidently will it be applied, and the more useful will it become.

There has, perhaps, in no other place been made such an extensive practical use of a formula of this kind as in the laboratory which is under my charge. In support of this assumption, I may remind you that in the bulk of the milk samples examined in my laboratory—about 18,000 annually—the percentage of fat is calculated from specific gravity and total solids. There are, however, gravimetric fat determinations also continuously being made, which allow the results of fat-extraction to be compared with those of fat-calculation. As, until a few months ago, Soxhlet's plaster process was the one employed, the formula constructed by Fleischmann was used for the calculation.

At the end of the year 1887 I extracted from my laboratory journals 628 analyses of whole and skim milks, in which the amount of fat varied from ten down to one-tenth of a per cent., and in which fat calculated differed from fat found from  $-0.2$  to  $+0.2$  per cent.; the average difference was  $+0.020$ . These results I communicated to the Society at the February meeting, 1888. (THE ANALYST, 1888, vol. xiii., p. 50).

I have now extracted some further figures, which allow a comparison of the results of fat-extraction to be made with those of fat-calculation, and thought it not undesirable to put them on record. For a reason which will be apparent later on, the analyses were divided into two classes; the first class comprising samples of ordinary, the



second samples of skim milk. The calculated figures compare with those actually found, as follows :—

| Year.      | Number of Samples. | Description.  | Maximum Differences. | Average Difference. |
|------------|--------------------|---------------|----------------------|---------------------|
| 1888       | ... 73             | ... Milk ...  | — 0·2 to + 0·2       | ... + 0·001         |
| „          | ... 143            | ... Skim Milk | — 0·2 „ + 0·2        | ... + 0·019         |
| 1889       | ... 55             | ... Milk ...  | — 0·2 „ + 0·2        | ... — 0·004         |
| „          | ... 119            | ... Skim Milk | — 0·2 „ + 0·2        | ... + 0·057         |
| 1890-91... | 143                | ... Milk ...  | — 0·4 „ + 0·1        | ... — 0·143         |
| „          | ... 207            | ... Skim Milk | — 0·3 „ + 0·1        | ... — 0·048         |

The same maximum differences, and an equally satisfactory close average agreement, as observed during the years from 1881 to 1887, were again found in 1888 and 1889 ; with regard, however, to analyses made during the period from January, 1890, to end of April, 1891, the fat calculated falls considerably behind the fat extracted. The explanation for this variation is easily found. In a very able paper read before this Society in the year 1889 (*THE ANALYST*, 1889, vol. xiv., p. 121), Richmond showed “that the difference between Adams’ method and Soxhlet’s method is the result of, on the one hand, extraction of something, not milk-fat, and on the other, incomplete extraction,” and recommended, as remedies in the one case, using paper previously extracted with acidified alcohol ; in the other, fine grinding and re-grinding of the dry mass consisting of plaster and milk solids, and prolonged extraction. The circumstance that an extracted paper was not to be had in the market deterred me from abandoning Soxhlet’s and adopting Adams’ method. In order, however, to ensure a more complete extraction, I altered my way of working the plaster process, in so far that, instead of 10 grammes of milk I dried 5 grammes only on the usual quantity of plaster of Paris, thereby doubling the surface over which the milk solids were spread. The result was that—looking at the average differences—the practically entire agreement disappeared, and the fat calculated fell considerably short of the fat actually found. This fact is more particularly noticeable in the case of ordinary milk samples, less so with regard to skim milks, proving that the differences between the plaster process, as worked in former days, and when worked with additional precautions, are increasing with the increase of fat. The same observation has repeatedly been made with regard to the plaster and paper processes. Why that should be so is still an unexplained mystery to me, for I cannot accept Richmond’s statement that the difference is only an apparent one, as of the total fat present, a higher percentage is left behind in the case of skim, a lower in the case of ordinary milk. The question is, in my opinion, not what proportion, but what actual quantity of fat is left behind, and it appears strange to me that this quantity should be larger where the conditions for extraction undoubtedly seem more favourable.

Since a fat-free paper has been introduced I have discarded the plaster and adopted the paper process for fat extractions. Results obtained by using the last-named process must, of course, be compared with figures calculated from *Hehner’s formula*. Such a

comparison has been possible in a number of analyses made from beginning of May to end of September of the present year, with the following results:—

| Year. | Number of Samples. |    | Description. | Maximum Differences.    | Average Difference. |
|-------|--------------------|----|--------------|-------------------------|---------------------|
| 1891  | ...                | 27 | ...          | Milk ... — 0·1 to + 0·2 | ... + 0·030         |
| "     | ...                | 70 | ...          | Skim Milk — 0·1 „ + 0·2 | ... + 0·060         |

I may remark that in a considerable number of analyses the agreement is absolute, or, speaking more correctly, the differences are below 0·05 per cent.

When the paper process was first brought out, it was stated that the greater facility which it offers for the complete extraction of the fat is due to the fact that the solid residue of the 5 grs. of milk used for the fat determination is spread over a surface of upwards of 5,000 square centimeters. This calculation is based on the assumption that the solids are uniformly distributed over all the fibres constituting the paper. But, already in the early days of the process, several observers, and later on, Richmond, in his paper to which I have referred, have drawn attention to the fact that the blotting-paper exercises a certain selective or separating action. This action is, I believe, only imperfectly understood. Milk serum, *i.e.*, milk minus fat, must not be considered a simple solution of various bodies in water. Part of the salts, the milk-sugar, and part of the proteids are certainly dissolved in the water in the usual sense of the term, but far the greater part of the proteids—the casein—in connection with the rest of the mineral matter is present in a kind of swollen state, resembling, but not identical with, solution. As far back as 1877 Professor Lehmann, of Munich, has made use of this for the quantitative determination of casein and fat. He proposed to pour a weighed quantity of a mixture of equal parts of milk and water on a porous clay plate, which would soon suck in the water with everything dissolved in it, leaving behind a pasty layer of casein and, enclosed in the latter, the fat. This mass was to be carefully removed while still damp, dried, and extracted, and fat and casein weighed. In the paper process, the blotting-paper takes the place of the clay plate; the watery solution sinks into it, and the casein encasing the fat is left on and near the surface. According to this theory, the fat is left in contact with only about one-third of the non-fatty solids, while about two-thirds, including the whole of the milk-sugar, are removed from it. That, under such conditions, extraction of the fat is made easier can be readily imagined. The practice of fat-extraction has received such a large share of attention lately, that I thought a few words on its theory might be found of some interest. Whether, with the introduction of the paper process, or some other method giving similar results, the question is definitely closed, I am not prepared to say.

In my paper "On the relation between specific gravity, fat, and total solids in milk," read in February, 1888, I stated that formula like Fleischmann's or Hehner's can be applied with satisfactory results, if ash, proteids, and milk-sugar are present in their normal relative quantities, namely, roughly speaking, in the proportion of 1 : 5 : 6. As these figures have been repeatedly quoted, I should like to take this opportunity for stating that, according to my experience, and not roughly, but speaking as correctly as

the case admits, normal milk contains ash, proteids, and milk-sugar in the proportion of 2 : 9 : 13.

#### DISCUSSION.

The Chairman (Mr. A. H. Allen) said that Dr. Vieth had had so extensive and varied an experience in the analysis of milk and milk-products, that anything he might say thereon must command the utmost attention of the members. The figures brought forward on this occasion were of value, as showing the great variations in the estimation of fat by the processes referred to, and the extent to which such estimations were to be trusted. It seemed to him, however, that the processes dealt with in the paper before them had lost the importance they once had in daily practice, and at the present day possessed only a historical interest. Much time and ingenuity had been spent in devising methods for extracting fat perfectly from milk and other bodies. They had endeavoured to attain that end by the use of plaster of Paris, sand, blotting paper, cotton-wool, etc.; but the Gordian knot had been at length cut, when Werner Schmid brought forward his method of estimating the fat by boiling the milk with hydrochloric acid and shaking out with ether. For his own part, he did not believe that anybody who had once fairly tried that method would ever use paper coils or plaster of Paris again for that purpose. The experience of those who had adopted Schmid's method was so satisfactory that all other fat extraction processes had been abandoned by them; and he could not but think that if Dr. Vieth would make a comparison between the two processes dealt with in his Paper, and this third method, he would agree with others that the former, after having done excellent duty in the past, were now either obsolete, or would soon become so, owing to the advantages possessed by the Schmid method.

Mr. Bodmer agreed with Mr. Allen's view, that when once an analyst had got into the way of working the Schmid process he would never again use a paper coil, or anything else, for fat estimation. In this connection, he would like to mention that he had recently applied the Schmid method to a sample of milk which struck him as looking somewhat yellow. On adding the hydrochloric acid, the milk turned a beautiful rose-pink colour. But for the Schmid process he would probably have had no evidence of this peculiarity. On attempting to extract the colouring matter, it became clear that the rose-colour was developed by a mineral acid only, and was obstinately retained by the casein; for, on adding a few drops of acetic acid, and thus curdling the milk, it remained colourless, and the serum did not re-act with hydrochloric acid. On adding hydrochloric acid, however, to the separated casein, the rose-colour was produced; the subsequent addition of an alkali discharged the red colour. No doubt the colouring matter was methyl-orange or some similar body.

Mr. Stokes agreed with Mr. Allen that Dr. Vieth's Papers were always interesting and valuable, the reason being that they were always based on actual facts. He had been specially interested by the figures resulting from the comparison of the two methods which the author had dealt with. He had made thousands of such comparisons himself, and his experience was that if the samples ran in an ordinary series, showing say, from

5.0 to 0.5 per cent. of fat, then any particular method of calculation would agree with the results obtained. But when higher or lower results were obtained, no process that he knew of would always agree with them closely. With regard to paper coils, etc., they might still be retained and sometimes used, but only, he thought, as curiosities, or as a means of checking the results got by the Schmid process. There could be no doubt as to the advantage of the latter over all other methods for the estimation of fats. Mr. Stokes then drew upon the blackboard and described an apparatus (a full description of which, he said, was to be found in the current number of the *Journal of the Chemical Society*\*), by means of which the inventor claimed that the Schmid process could be actually performed in 30 minutes. He also exhibited some specimens of flat glazed porcelain dishes, which he had found especially suitable for milk analyses in place of platinum. These differ from the ordinary flat porcelain dishes in having every part, including the bottom, glazed; so that no dirt can stick to them. They were specially made for Messrs. Townson & Mercer.

Mr. Harvey admitted that he had not yet tried the Schmid process, chiefly because he was averse to pipetting an ethereal solution at the ordinary temperature of the laboratory. It seemed to him that such a practice was likely to result in not getting accurate results due to the loss of ether. He would be glad to know whether it was practically possible to work the Schmid process so that the *whole* of the ether employed could be evaporated, and on weighing, the whole of the fat obtained.

Mr. Stokes reminded the last speaker that Mr. Allen had, at a previous meeting, described a wash-bottle by means of which the ether could be drawn off and used over and over again without loss, it being necessary, however, at each operation to wait for the ether to settle. With regard to the difficulty of pipetting ether referred to, he would guarantee to carry ether in a pipette the length of the Lecture Room without loss, provided a little fat were present.

The Chairman, in proposing a vote of thanks to Dr. Vieth for his Paper, took the opportunity of saying what he had omitted from his former remarks, namely, that although the method in question had originated with Werner Schmid, they were indebted to Mr. Stokes for bringing it before the notice of that Society, and advocating it on many occasions. He in no way intended to impugn the paper-coil and plaster methods, both of which he believed were excellent in their way, and in certain laboratories might be found more convenient than the Werner Schmid process; but in his experience the last was quite as accurate, more rapid, and less troublesome. Mr. Harvey had probably not been present at a previous meeting when he (Mr. Allen) described an arrangement for avoiding the necessity of taking an aliquot part of the ether. Mr. Allen then made a sketch, and gave a description of the apparatus constructed by Mr. Chattaway for the purpose of drawing off the ethereal liquid instead of pipetting it in the usual way. With regard to the dishes exhibited by Mr. Stokes, he might say that he had often used dishes of the same shape for many years past for evaporation in preference to platinum. He

\* (See abstract in this Journal, page 209.)

found that no sensible alteration of weight occurred; the basins always dried back to their original weight within a milligramme, and could be ignited with perfect safety. They had this advantage, the weight and other characters could be written on them with black-lead pencil. The dishes he had used, however, were unglazed externally, and he was glad, therefore, to learn that they could now be obtained enamelled both inside and outside.

Mr. Bernard Dyer enquired whether such dishes were suitable for ash determinations?

Mr. Allen replied that they were.

Mr. Stokes preferred to use platinum for that purpose, as he found that with porcelain dishes the operation took too long a time.

Dr. Vieth, in reply, said that there was only one point to which he need refer. Mr. Stokes has said that in the case of samples containing more than 5 per cent. of fat he would not expect any formula to give results agreeing with the figures actually found. While he admitted that that was true to some extent, he also believed that in such cases duplicate analyses would not be found to agree so well as Mr. Stokes would wish.

The following description of two forms of apparatus for the removal of an ethereal layer, without loss, has been kindly forwarded by Mr. Allen, and will be read with interest in connection with the preceding paper. They are from an advance sheet of the third volume of the new edition of Mr. Allen's Commercial Organic Analysis, which is now in the press:—



Fig. 1.

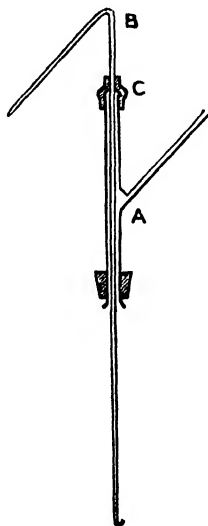


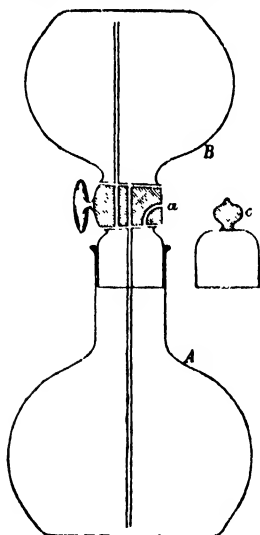
Fig. 2.

"When the volume of fluid treated with immiscible solvent is small, the syringe pipette shown in fig. 1 may be conveniently employed. It is readily constructed by drawing out a test-tube, so as to form a narrow prolongation, the orifice of which should be turned up so as not to disturb the liquid in which it is immersed. A narrow test-tube, fashioned into a handle at the upper part, serves as a piston, a short length of india-rubber tubing uniting it to the outer tube, while allowing easy movement up and down.

"Another convenient form of separator, devised by W. Chattaway, is shown in fig. 2. It is practically a small wash-bottle fitting, which is adjusted to the tube or cylinder containing the layers of liquid it is desired to separate. It is so arranged that the exit-tube (B) can be adjusted in height by sliding it through the india-rubber collar C, so as to bring the turned-up end just above the junction of the two layers. On

then blowing through the side-tube (A), the upper stratum is forced up the inner tube, and can be removed, almost to the last drop, without disturbing the lower layer."

**Apparatus for the Estimation of Fat in Milk.** E. Molinari (*Berichte Deutsch. Chem. Gesell.* 24, p. 2204). The author, after criticising the various methods for estimating fat in milk which have been proposed from time to time, agrees with Stokes (ANALYST, 1885, p. 48), Eustace Hill (ANALYST, 1891, p. 67), and Bondzynsky (*Landwirth Jahrb. der Schweiz*, 1889), that the method of Werner Schmid is the simplest, most rapid, and convenient hitherto introduced. The conditions tending to inaccuracy are:—the employment of ether containing alcohol; boiling the mixture of milk and acid too long, when a caramel-like body is formed, soluble in ether; the difficulty of reading off the volume of ether left in the tube, owing to the gradations of the instrument being obscured by the flocculent layer of casein; when only a portion of the ether is used, fat may be left behind in the acid mixture, as shown by Allen (*Chem. Zeit.*, 1891, p. 331). The author believes that by the invention of the simple apparatus represented in the accom-



ppanying figure, he has rendered the process both accurate and convenient. This consists of a flask B of about 75 c.c. capacity, which has a glass tap fused on, with two capillary tubes attached, the one passing upward the other downward. The neck of flask B is ground into the neck of flask A, which holds about 90 c.c. Either of the flasks can be placed in communication with the external air by the opening *a*. The ether must be previously washed with one or two tenths of its volume of water, to remove traces of alcohol. The operation is performed as follows:—10 c.c. of well-mixed milk are weighed in (or measured into) flask A, 10 c.c. of hydrochloric acid added, and the mixture heated to boiling on an asbestos sheet. The boiling must not exceed a minute and a half, the fluid being shaken from time to time, and not allowed to become of a deeper colour than a dark-brown [not black]. The flask is cooled, and 25 c.c. of ether added. The two flasks are connected as shown in the

figure, the tap closed, and the whole shaken for a few minutes, the flask being vented two or three times by the opening *a*. The apparatus is now inverted, allowed to stand five or six minutes, the tap turned, and the dark acid liquid drawn off into flask B. By a little shaking of the ether the whole of the acid liquid may be easily got into the lower flask. The apparatus is again inverted, then separated, 10 c.c. of ether are introduced into flask B, the tap closed, and the fluids well shaken. When the ether layer is distinct, the acid liquor is run off, and the ether solution transferred to A. The whole of the ether solution is washed in the apparatus two or three times with a little water, the flask A removed to the water-bath, the ether driven off, the last traces of ether and water being removed by placing the flask in a drying oven heated from 107 to 110°C., where it must remain at least 20 minutes. The usual cooling in the exsiccator and weighing concludes the operation. Examples are given showing its concordance with the Adams' and other recognised processes. Sour milk, which must be

weighed in the flask, can be conveniently analysed; also cream, using 5 grms. cream and 10 c.c. hydrochloric acid.

W. J. S.

**Determination of Citric Acid in Wine.** A. Klinger and A. Bujard (*Zeitsch. f. angew. Chem.* 1891, p. 514).—In testing wine in accordance with the Nessler-Barth method, a sample of wine yielded a precipitate of the calcium salt which, on being further tested, was found to be the malate, and not citrate. On investigating the matter, the authors found that malate of calcium is precipitated by boiling from its nearly neutral solution in the same manner as citrate. To distinguish between the two salts, the following method is recommended: At least 250 c.c. of the wine to be tested are evaporated to about one-third of its bulk. Potassium acetate is then added, the solution strongly acidulated with acetic acid, and a double bulk of strong alcohol added. This throws down the tartrate. After twenty-four hours the precipitate is filtered off, washed with a few c.c. dilute alcohol. The filtrate is precipitated with basic lead acetate, the precipitate being also washed with alcohol, it is then decomposed with hydrogen sulphide.

The filtrate from the lead sulphide is concentrated and made alkaline with lime-water. The precipitate, which consists of phosphate and a trace of tartrate, filtered off after a few hours. The solution is rendered acid with acetic acid, and evaporated to dryness. The residue is dissolved in a little hot dilute hydrochloric acid, and after addition of some ammonium chloride, is made faintly ammoniacal, and boiled for some length of time, when only citrate will be precipitated, and no malate.

O. H.

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**The use of the principle of the Separator in Analytical and Microscopical Work.** W. Thorner (*Chem. Zeit.* 1891, 15, 1201–1203).—The author has experimented with the separator as a means for the analysis of meal and butter; an extension of its familiar use for milk in the case of the lactocrite. The instrument chosen was that known as the "Victoria," by Watson, Laidlaw & Co., of Glasgow. It is arranged to give a speed of 6,000–7,000 revolutions per minute easily.

(1.) *Experiments with various meals and starches.* One gramme of the material to be tested is shaken with a suitable liquid—*e.g.*, water, alcohol, or ether, in a tube, the lower part of which is very narrow, and divided into  $\frac{1}{16}$  c.c. The capacity of the whole tube is about 15 c.c., and that of the narrow part 3 c.c. The tube is filled with liquid to within about 2 cm. of the upper edge, and well shaken, to mix the substance to be examined with the liquid. It is then placed in the centrifugal machine, a plate 350 mm. in diameter being used, and driven at 2,000–2,500 revolutions per minute for five minutes. The

following numbers are the mean of several concordant results obtained by this method :—

| Material.       | Percentage of Water. | Liquid used. |          |        |
|-----------------|----------------------|--------------|----------|--------|
|                 |                      | Water.       | Alcohol. | Ether. |
| Wheat flour I.  | 14.6                 | 14.3         | 16.6     | 15.2   |
| „ II.           | 14.6                 | 14.5         | 16.5     | 15.6   |
| „ III.          | 14.6                 | 15.3         | 16.0     | 15.0   |
| Rye flour I.    | 14.0                 | 30.0         | 16.4     | 16.0   |
| „ II.           | 14.0                 | 30.0         | 16.0     | 15.7   |
| Oat flour       | 11.9                 | 30.0         | 17.8     | 17.0   |
| Barley flour    | 12.5                 | 22.0         | 16.5     | 14.0   |
| Pea flour       | 17.6                 | 22.4         | 20.6     | 18.0   |
| Buckwheat flour | 14.8                 | 19.5         | 15.8     | 15.5   |
| Rice flour      | 13.8                 | 19.8         | 14.2     | 13.9   |
| Rice starch     | 15.0                 | 12.6         | 15.8     | 15.8   |
| Potato starch   | 11.1                 | 13.3         | 11.0     | 12.0   |
| Mondamin        | 14.1                 | 13.6         | 12.0     | 12.4   |

The numbers in the last three columns are the tenths of a centimeter occupied by the flour after being subjected to centrifugal action.

The results got by the use of alcohol and ether are too similar for all the various materials tried to make the use of these liquids valuable, except when it is desired to make several tests under different conditions upon the same sample. With water, on the other hand, the differences are sufficiently considerable to allow of the different flours and starches being readily distinguished. Especially is this the case with rye flour (see table)—a fortunate circumstance, as it is frequently used as an adulterant of the more costly wheat flour. The following table shows the results obtained with known mixtures of wheat and rye flour :—

|                  |                |     |     |     |     | Height in $\frac{1}{16}$ c.c. |
|------------------|----------------|-----|-----|-----|-----|-------------------------------|
| Pure wheat flour | ..             | ... | ... | ... | ... | 14.3                          |
| 90 % wheat flour | 10 % rye flour | ... | ... | ... | ... | 15.2                          |
| 80               | 20             | ..  | ... | ... | ..  | 16.3                          |
| 70               | 30             | ..  | ... | ... | ... | 17.7                          |
| 60               | 40             | ..  | ... | ... | ... | 18.6                          |
| 50               | 50             | ..  | ... | ... | ... | 20.4                          |
| 40               | 60             | ..  | ... | ... | ... | 21.2                          |
| 30               | 70             | ..  | ... | ... | ... | 23.2                          |
| 20               | 80             | ..  | ... | ... | ... | 26.0                          |
| 10               | 90             | ..  | ... | ... | ... | 28.5                          |

The wheat flour contained 14.6 per cent. of water, and the rye flour 14.0 per cent. In order to avoid fluctuations, due to different amounts of water, it is preferable to conduct



the experiments with samples dried at 100–102° c. to constant weight. The results do not, however, differ greatly from those obtained with the undried samples, as is shown by the following figures :—

| Material.       |     |     | Liquid used. |          |        |
|-----------------|-----|-----|--------------|----------|--------|
|                 |     |     | Water.       | Alcohol. | Ether. |
| Wheat flour I.  | ... | ... | 15.4         | 18.0     | 15.2   |
| Rye „ I.        | ... | ... | 33.0         | 19.0     | 17.0   |
| Oat „           | ... | ... | 30.0         | 18.5     | 16.2   |
| Barley „        | ... | ... | 22.8         | 17.5     | 15.2   |
| Pea „           | ... | ... | 25.3         | 18.3     | 16.5   |
| Buckwheat flour | ... | ... | 22.8         | 17.0     | 16.0   |
| Ground rice     | ... | ... | 23.8         | 17.6     | 14.0   |
| Rice starch     | ... | ... | 15.0         | 17.0     | 16.0   |
| Potato „        | ... | ... | 16.8         | 12.0     | 12.0   |
| Mondamin        | ... | ... | 15.3         | 13.7     | 13.7   |

The results, as before, are given in tenths of a c.c.

Mixtures of wheat and rye flour gave the following results :—

| Wheat flour. | Rye flour. |  | Liquid used. |                              |
|--------------|------------|--|--------------|------------------------------|
|              |            |  | Water.       | 90 % water and 10 % alcohol. |
| 100 %        | — %        |  | 15.4         | 15.2                         |
| 90           | 10         |  | 17.5         | 16.0                         |
| 80           | 20         |  | 18.0         | 17.0                         |
| 70           | 30         |  | 20.0         | 18.0                         |
| 60           | 40         |  | 21.5         | 19.6                         |
| 50           | 50         |  | 22.9         | 22.0                         |
| 40           | 60         |  | 24.0         | 23.2                         |
| 30           | 70         |  | 25.5         | 24.0                         |
| 20           | 80         |  | 28.0         | 25.0                         |
| 10           | 90         |  | 30.5         | 27.0                         |
| —            | 100        |  | 33.0         | 30.0                         |

These figures confirm those given above, and indicate that a determination of the percentage of rye flour in wheat flour containing this adulterant is quite practicable. The process would probably give equally definite indications with oat-flour. Instead of weighing a portion of the sample, sufficient exactitude could probably be obtained by measuring it in a little glass vessel with a ground cover. This is a suggestion which the author has not yet verified.

The presence of mineral adulterants, such as chalk and barytes, can be detected by the same process, the volume occupied by the flour diminishing as the percentage of mineral matter increases. A neater method consists in using chloroform instead of water as a separating liquid, and after shaking, adding  $\frac{1}{2}$  — 1 c.c. of water, shaking again and revolving in the separator, almost complete separation takes place, the flour floating on

the chloroform layer, and the heavy mineral adulterant sinking to the lower graduated part of the tube, where its bulk can be read off. The microscopical examination of meal and flour, and the isolation of the husk residue from them, can be aided by the use of the separator. 5 grms. of the sample are treated with 500 c.c. of water on the water-bath. 100 c.c. of the mixture are then heated for ten minutes on the water-bath with 5 c.c. of glacial acetic acid, and another portion of 100 c.c. similarly treated with 1 c.c. of caustic potash solution (1:2). Both are then revolved for five minutes, and the residue at the bottom of the tube separated and examined under the microscope.

(2). *Application of the method to the analysis of butter.* A quantity of the butter to be tested is measured by means of a glass cylinder, closed at each end by a glass plate ground to fit. The cylinder is just small enough to enter the wider and upper part of the separator tube, so that its contents (10 c.c. = 9.5 grms. of normal butter) can be transferred thereto. The separator tube is revolved on a plate 360 mm. in diameter for 2-3 minutes at a speed of about 2,000 revolutions per minute. The matter, other than butter fat, collects in the narrow, graduated, lower part of the tube, generally in two layers, the upper consisting of water in which some casein is suspended, the lower also of water, but almost clear, save for such insoluble mineral matter, flour, and starch that may be present. Crystals of salt may also occur. The total watery layer represents the amount of butter milk in the sample. The whole operation can be completed in ten minutes. The separator tube differs from that previously described, only in having an enlargement on its upper part, so as to support it in the water-bath during the introduction of the fused butter from the measuring cylinder.

The insoluble fatty acids can be determined by measuring 1 c.c. of butter-fat at 100 c.c. into a separator tube with the middle part contracted, and graduated to  $\frac{1}{10}$  c.c. saponifying therein, driving off the alcohol, acidulating, revolving in the centrifugal machine, and reading off the volume at a temperature of 100 c.c. The data thus collected, together with the refractive index determined in the usual way, suffice to arrive at a fair judgment of the quality of the sample with great expedition.

B. B.

**Method for the determination of the Fat in Sour Milk by means of the Lactocrite of De Laval.** M. Ekenberg (*Chemische. Zeit.*, 1891, 15, 1239).—In carrying out the examination of milk it often happens, in summer time, that the samples become sour during transport, in which case it is a matter of extreme difficulty to obtain a portion for analysis representative of the whole. When decomposition has proceeded so far that the milk is already coagulated, it is utterly impossible to mix the layer of cream (the fat) uniformly with the whey.

A reliable method for analysing sour milk has hitherto been lacking. In the laboratory of the Actiengesellschaft Separator, at Stockholm, various investigations have been made for some time since to apply the lactocrite to the examination of sour milk,

whereby it was proved that sour milk could be made to give results as certain as those got with fresh milk, in that thoroughly uniform samples could be obtained and accurate measurement was possible.

Seeing that, as has been already noted, it was impossible to mix the fat with the rest of a sample of sour milk merely by shaking, a substance was sought which should be without action on the fat, but capable of restoring the milk to its normal consistency. The result of the experiments in this direction was, that if ordinary ammonia (5 per cent. by volume) was added to the sour milk and the mixture shaken, it became quite fluid, and the fat could be determined in the same manner as in an ordinary milk. On examining a sample immediately after treatment under the microscope, it was seen that the fat globules were equally disseminated throughout it. This was further substantiated by a series of experiments with the lactocrite, using the new "lactocrite acid," *i.e.*, lactic acid mixed with hydrochloric acid. (*See THE ANALYST*, 1891, p. 135.)

The method of conducting the experiments and the results given by them were as follows :—

100 c.c. of whole milk were measured out into each of four clean dry flasks. The fat, as determined by 6 tests with the lactocrite, amounted to 3.22 per cent. The flasks were numbered, well closed, and kept completely free from disturbance at a temperature of 18° to 23°C.

After 24 hours the milk in all the flasks was sour and coagulated. After a further period of 24 hours 5 c.c. of ammonia were added to the contents of flask No. 1, and the mixture well shaken, a thin fluid product, from which portions for testing by the lactocrite could be easily measured off, being obtained. Six tests were made and gave the following results :—3.00 per cent., 3.00 per cent. 3.01. per cent., 3.02 per cent., 2.99 per cent., and 2.99 per cent., the average being 3.00 per cent., corresponding to an amount of fat in the milk of 3.15 per cent.—that is  $\frac{100}{32}$  of the amount of fat given by the sample to which ammonia had been added. After 5 days flask No. 2 was examined in the same way as No. 1. The mixture in this gave by the lactocrite test a content of fat of 2.90 per cent., 2.90 per cent., 2.90 per cent., 2.90 per cent., 2.92 per cent., corresponding to an amount of fat in the milk of 3.05 per cent. Flask No. 3 gave, after the elapse of 7 days, 2.84 per cent., 2.84 per cent., 2.85 per cent., 2.85 per cent., 2.83 per cent., 2.84 per cent., an average of 2.84 per cent. corresponding to a percentage of 2.98 per cent. of fat in the milk. Flask No. 4 was examined after 9 days, and gave 2.82 per cent., 2.83 per cent., 2.84 per cent., 2.83 per cent., 2.82 per cent., an average of 2.83 per cent., corresponding to 2.97 per cent. of fat in the milk.

On comparing the results of 5 or 6 determinations of the fat in the mixture of milk and ammonia in each flask among themselves, it is seen that the layer of cream which had separated previous to and during the souring of the milk, had become thoroughly mixed by shaking, after the addition of 5 per cent. of ammonia. On comparing the results of the different flasks with each other, it is evident that the longer the sour milk stood, the lower was the fat as determined by the lactocrite. That the fat decomposes on keeping the milk is well known, and this fact explains why the result of a

determination with the lactocrite is lower as the age of the sample increases. The sooner the sour milk is treated with ammonia, and tested with the lactocrite, the better the result. When the samples are only 1 to 2 days old—and older samples should not often have to be examined—this tendency is of negligible importance, as is shown by the foregoing figures.

Further experiments have proved that the diminution in the result of the determination of the fat in sour milk which was two days old, by means of the lactocrite, averaged 0.05 per cent., wherefore this number should be added to the percentage found. Thus the percentage of fat found in the foregoing investigation in flask No. 1 was 3.15 per cent., which, when increased by the addition of 0.05 per cent., becomes 3.20 per cent., while the fresh milk had, as already noted, 3.22 per cent. of fat. As no perceptible ill effect is to be feared from the addition of 5 per cent. of ammonia, especially when the sample is examined by the lactocrite immediately after the addition, the plan of adding ammonia to sour milk is much to be recommended.

In order to obtain a reliable result, the volume of the sample to be tested must be ascertained before the addition of the ammonia, because after the milk has become sour, the cream separated, and the milk coagulated, no average sample for admixture with 5 per cent. of ammonia can be measured off. The ammonia must be added to the sample in the vessel in which it has become sour.

B. B.

**The Analytical Use of Barium Dioxide and Hydrogen Dioxide.**  
E. Donath (*Chem. Zeit.*, 1891, 15, 1085, 1086).—The author, after claiming priority in the use of barium dioxide in attacking chrome iron ore, which he considers has been erroneously ascribed by Baumann to Kinnicut and Patterson, enumerates some of the advantages it possesses. The ore is completely attacked if about ten times its weight of the dioxide be used, even when heated only over a bunsen burner, provided the dioxide be of good quality. Commercial samples leave much to be desired in this respect. The mass does not fuse, and is therefore more easily removed from the crucible than when sodium carbonate is added, as by Kinnicut and Patterson; moreover, the use of the alkali causes a portion of the chromium to remain as chromic oxide, which has to be oxidised to chromate by hydrogen peroxide.

The author has also used the dioxide with success in attacking slags, lead-glasses, and clays, as well as minerals containing chromium.

The usual method of determining the chromate formed from chrome iron ore by any process of oxidising attack with ammonio-ferrous sulphate, and estimating the excess of the latter by permanganate, is, in the author's opinion, inferior to the plan of determining it by titration of the iodine liberated by its action upon potassium iodide in hydrochloric acid solution with sodium thiosulphate.

Hydrogen dioxide is an excellent oxidant for ferrous salts in acid solution, and excess is more easily removed than is the case with such substances as potassium chlorate, nitric

acid, or bromine. It can be used with good effect for getting rid of ammonium sulphide without separation of sulphur, and for oxidising an ammoniacal solution of sulphide of arsenic (such as is obtained in the separation of antimony, arsenic, tin, etc.) to ammonium arseniate, prior to precipitation with magnesia mixture. The oxidising effect of hydrogen dioxide in alkaline solution is comparatively weak, being less energetic than that of bromine or potassium permanganate. Thus, nickel hydrate is quickly oxidised by bromine to the peroxide, but is unaffected by hydrogen dioxide; in this respect the latter reagent is similar to iodine.

B. B.

**On the Influence of the so-called Nitrogen-free Extractive Matter on the Result of the Estimation of Starch in Cereals.** C. J. Lintner and G. Düll. (*Zeit. f. angew. Chem.* 1891, p. 537).—The authors show in a paper (1. c. p. 538) that the gum-like body found in barley some time since by Lintner, yields upon hydrolysis Galactose and Xylose, the former being fermentable with great difficulty, the latter unfermentable. Both re-act with Fehling's solution, and therefore interfere with the accuracy of an ordinary starch determination. To ascertain the amount of error caused by the presence of this body, a number of experiments were made; 3 grammes of the finely powdered substance were heated for 3 hours with 75 c.c. of water in a digester at a pressure of 3·5 atmospheres, filtered through glass wool, 15 c.c. hydrochloric acid s.g. 1·125 added, and the whole made up to 200 c.c. with water. This was inverted in the water-bath for 3 hours, neutralised, made up to 500 c.c., and a sugar estimation made on 25 c.c. by Allihn's method. For the calculation dextrose to starch, the factor 0·9 was used. The remainder of the solution, after concentration, was fermented with a little pressed yeast, made up to 100 c.c., and the reducing matters determined in an aliquot part by Allihn's method. The fermentation removes the whole of the dextrose, a small portion of the galactose, and leaves the xylose intact. In this way the following figures were obtained:—

| I.           |            | II.  |
|--------------|------------|--|
| Starch       |            | Unfermentable reducing matters reckoned as Starch. |
| Barley       | 56·86 p.c. | 2·7 p.c.   |
| Wheat        | 56·27 p.c. | 4·0 p.c.   |
| Maize        | 62·50 p.c. | 1·5 p.c.   |
| Potato Flour | 65·03 p.c. | 2·0 p.c.   |

If the figures in column II. are deducted from those in column I., the difference will be the amount of starch actually contained in each sample, *i.e.*, provided the factor employed (0·9) is the correct one. Sachsse (*Chem. Cent.* 1878, p. 732) states that the relation of dextrose to starch is not 100 : 90 but 108 : 99, giving the factor 0·917; Soxlet (*W. Brauer*, 1885, p. 193) after much investigation (and probably working under slightly different conditions), gives 0·94. The authors working in the following manner, come to

the conclusion that 0.941 is the correct factor; 3 grms. of starch, 15 to 20 c.c., hydrochloric acid s.g. 1.125, water 200 c.c., time of inversion 3 hours. Special stress is laid upon the point, that the mixture should be well shaken to ensure thorough diffusion of the starch through the fluid, otherwise a yellow colour appears, showing partial destruction of sugar. Consequently, to arrive at the truth as near as possible, the difference between columns I. and II. should be multiplied 0.94. The figures then respectively stand 56.57, 54.59, 63.18, and 66.32, and do not materially differ from those of column I. Hence, by neglecting the influence of the gum, and employing a slightly inaccurate factor, the two errors nearly counterbalance one another; and for the estimation of starch in cereals this method may be employed. In the case of bran, brewers' grains, &c., which contain large amounts of nitrogen-free extractive matter, the result would be very inaccurate. If the estimation be one of a pure starch, then the factor 0.94 must be employed.

W. J. S.

**The Determination of Lead in Tin Plate Vessels used for Canned Goods.** J. Pinette (*Chem. Zeit.* 15, 1891, 1109).—The exact limit for lead in the covering of tin plate used for vessels containing preserved food, and in their soldered seams, being proscribed by law in Germany, its determination is of some moment. Although no such regulation exists in this country, the intrinsic importance of the question is as great. The plan suggested consists in avoiding the troublesome process of scraping off the tin from the sheet iron, and in simply acting upon fragments of the vessel with dilute nitric acid until the iron is laid bare and determining the tin and lead in the solution, the latter being dissolved as nitrate, the former chiefly remaining as meta-stannic acid. As it is only of importance to ascertain the ratio of tin to lead this plan suffices; it assumes, however, that the tin plate is coated with the same alloy on both sides. The fact that some iron is also dissolved is of no moment. The examination of the solder presents no difficulty, but it must be remembered that its composition may vary at different parts of the same vessel, that used for finally closing the "tin" after sterilization being usually richest in lead on account of its greater fusibility, and consequent ease in working. A can of American fruit was tinned with an alloy containing 0.55 per cent. of lead; its solder under the lid contained 50.84 per cent. Another of corned beef gave imponderable traces of lead in the tinning, and 50.06 per cent. of lead under the cover.

B. B.

**The Origin of Citric Acid in Milk.** A. Schelbe (*Landw. Versuchstat.*, 1891, 153, through *Chem. Zeit.*).—With ordinary fodder citric acid occurs in goat's milk as in cow's milk to the extent of 1—1.5 grammes per litre, but the amount is liable to considerable fluctuations, being sometimes double as great as at others (calculating it upon the total solids). It does not appear to be derived from the citric acid present

ready formed in the fodder, as it also occurs, though in smaller quantity, in human milk. Moreover, citric acid added to the fodder does not increase the amount found in the milk, and feeding exclusively upon materials free from citric acid, has no effect upon the quantity excreted. Milk secreted in a state of hunger contains the normal amount of citric acid.

Citric acid in milk is apparently not derived from the cellulose undergoing digestion in the intestines of herbivoræ as excretion goes on when food is withheld or meal substituted for ordinary fodder; this is consistent with the fact that in the human subject (where no digestion of cellulose takes place) 0.54—0.57 grammes of citric acid per litre of milk is formed.

B. B.

**Citric Acid as a Normal Constituent of Milk.** T. Henkel (*Landw. Versuchsstat.*, 1891, 134, through *Chem. Zeit.*).—The author's investigations as to whether citric acid occurs normally in cows' milk, or is formed from other constituents during the process of isolation, prove that its presence is not adventitious or occasional, but normal and constant.

B. B.

**Testing Metallic Iron for Arsenic.** O. Sautermeister (*Chem. Zeit.* 15 1891, 1021, 1022.)—The author examining various samples of iron for arsenic by the method prescribed in the German Pharmacopœia, which consists in dissolving 1 gramme of the metal in dilute hydrochloric acid and testing the hydrogen evolved by kindling it and allowing the flame to play upon a porcelain dish, as in Marsh's test, found that no reaction was given even when as much as 0.1 gramme of  $\text{As}_2\text{O}_3$  was purposely added. As a copious deposit was obtained when zinc was substituted for iron, it was evident that the latter had some specific action preventing the evolution of arseniuretted hydrogen. An examination of the residue unattacked by the acid showed the arsenic to be present there, having been reduced to the metallic state. The phenomenon was noticed by Wöhler and recorded by him in the *Annalen der Pharmacie* in 1839, but has apparently been since overlooked. The test can be amended and made useful by the addition of zinc (about 5 grammes of zinc to 2 grammes of iron), 1 milligramme of arsenic being then detectable. The arsenic does not come off at first, being only evolved when the liberation of hydrogen is taking place freely. An attempt to devise a method for the separation of arsenic and antimony, based upon the tendency of iron to precipitate the former metal in an acid solution, was frustrated by the fact that antimony behaves in exactly the same way. That the author's observation is not superfluous is proved by the detection of arsenic in samples of iron, which would have been wholly overlooked by the stereotyped method.

B. B.

**Preparation of Hydrogen Peroxide.** L. Crismer (*Bull. Soc. Chim.*, 1891, 3, 24, through *Chem. Zeit.*).—The process depends on the well-known property of hydrogen peroxide of dissolving in ether. Commercial barium dioxide containing 85—90 per cent.  $\text{BaO}_2$  is dissolved in a slight excess of hydrochloric acid of sp. gr. 1.10, and the solution shaken with an equal bulk of ether. After separation the ether is shaken with a little water, which removes the hydrogen peroxide which it had taken into solution. After separating the aqueous layer, the ether is again shaken with the same solution of barium dioxide, and once more extracted with water. After 5—6 operations the extraction is complete. A solution of hydrogen peroxide containing 8—9 per cent.  $\text{H}_2\text{O}_2$  perfectly neutral, and free from solid matter may be thus obtained.

B. B.

**Hübl's Iodine Absorption Method.** Holde. (*Mitt. König. tech. Versuchs.* 1891, 9, 81, through *Chem. Zeit.*).—The author endeavoured to ascertain the causes of, and remedies for, the discrepancies sometimes observed in determining the iodine absorption numbers of oils. As the result of his experiments he recommends the following procedure:—0.3 gramme of a non-drying oil or 0.2 gramme of a drying oil is weighed out and dissolved in 18—20 c.c. of chloroform in a flask (presumably stoppered) of about 300 c.c. capacity. 50 c.c. of Hübl's reagent, not more than fourteen days old, for a non-drying oil, and 60 c.c., not more than eight days old, for a drying oil are then added. (Two tests are made of each oil). The Hübl solution is allowed to act for two hours; 50 c.c. of the solution are titrated with sodium thiosulphate after the addition of 40 c.c. of 10 per cent. solution of potassium iodide, at the beginning of the determination, and 50 c.c. are kept in a well-closed flask until the determination is completed, and then titrated in the same manner, the mean of the two estimations being taken as the true value. The iodine unabsorbed by the oil is similarly determined after the addition of 40 c.c. of 10 per cent. solution of KI for a non-drying, and 50 c.c. for a drying oil, and 120 c.c. of water. Should the chloroformic solution of the oil become turbid while standing, more of the solvent must be added. The following are some of the results obtained:—Linseed oil, 172—180; hempseed oil, 175—176; walnut oil, 139—143; sesame oil, 106—109; cotton-seed oil, 110—115; crude rape oil, 100—108; refined rape oil, 100—107; arachis oil, 91.2—101.5; olive oil, 79—84; bone oil, 59.1—81.7.

B. B.

**Note by Abstractor.**—It is known to most analysts dealing with oils that a period longer than two hours is desirable to ensure full absorption, and that the alcoholic solutions of iodine and mercuric chloride which constitute when mixed Hübl's solution, are best kept separate and mixed only when wanted. The great loss of strength observed in Hübl's solution on keeping is thus avoided.



**Determination of the Ash in Sugar.** Albert and Hempel (*Deutsch. Zuckerind.*, 1891, 16, 1069, through *Chem. Zeit.*).—6—7 grammes of coarsely-ground quartz sand are placed in a platinum dish holding about 35 c.c., ignited, weighed, and mixed with 5 grammes of the sugar by means of a thin platinum wire. The mixture is ignited in a platinum muffle for a time, varying from  $\frac{1}{2}$  to  $1\frac{1}{2}$  hours. In the case of molasses 3 grammes are mixed with 12—15 grammes of sand. The ash is free from carbonates, and contains the quantity of sulphates and chlorides naturally present in the original sample, as is proved by analyses of commercial products and by experiments on known mixtures. A determination can be made as quickly as by the sulphate method, and involves no assumption as does that process. A disadvantage is that the platinum dish is perceptibly attacked; gold-plated vessels would probably do better. The moisture can previously be determined on the same portion; the difference between the weight of the dried sample and that of its ash gives the weight of the organic constituents direct, without the error caused by the presence of a portion of the carbon being left as carbonate in the ash and reckoned with it.

B. B.

## LEGAL.

**The New French Law regulating the Sale of Wine.** (*Journ. Officiel*, July 11th, 1891), includes the following provisions:—

Sect. 1. The product of fermentation of the husks of grapes from which the must has been extracted with water, with or without the addition of sugar, or mixed with wine in whatever proportion, may only be sold, or offered for sale, under the name of husk-wine, or sugared wine.

Sect. 2. The addition of the following substances to wine, husk-wine, sugared wine, or raisin-wine will be considered an adulteration:—

1. Colouring matters of all descriptions.
2. Sulphuric, nitric, hydrochloric, salicylic, boric acid, or similar substances.
3. Sodium chloride beyond one gramme per litre.

Sect. 3. The sale of plastered wines, containing more than two grammes of potassium, or sodium sulphate, is prohibited.

Offenders are subject to a fine of 16 to 500 francs, or to imprisonment from 6 days to 3 months, according to circumstances.

Barrels or vessels containing plastered wine must have affixed a notice to that effect in large letters, and the books, invoices, and bills of lading must likewise bear such notice.

O. H.

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ERRATA in Mr. Allen's Paper on the Assay of Aconite, p. 188:—

Line 20, for "grammes" read "milligrammes."

Line 25, for " $\frac{N}{10}$  baryta" read " $\frac{N}{50}$  baryta."

Line 27, for "12.14 milligrammes of japaconitine" read "12.44 milligrammes of japaconitine saponified."

Line 31, for "21.8 against 30 milligrammes taken" read "29.8 against 30 milligrammes taken."

In foot-note, for "76.7 mgrs. taken" read "7.67 mgrs. taken."

# THE ANALYST.

DECEMBER, 1891.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A MEETING of the Society of Public Analysts was held on the 4th November, 1891, the President being in the chair.

The minutes of the last meeting having been read and confirmed, Mr. Edgar B. Kenrick, of Winnipeg, Manitoba, was elected a member of the Society.

The following gentlemen were duly proposed :—

As member :—Dr. W. R. Smith, Public Analyst for Woolwich and Plumstead.

As associate :—Mr. E. H. Roberts, Assistant to Mr. Bernard Dyer.

The Secretary then read the following paper :—

### NOTE ON TABARIE'S PROCESS FOR THE INDIRECT DETERMINATION OF ALCOHOL.

By THOMAS P. BLUNT, M.A.

I HAVE used Tabarie's method for several years as a check upon the distillation process in the analysis of wines and beers, and have found the results approximate very closely. Allen describes the process in his *Commercial Organic Analysis*, volume 1, page 71, and makes the observation that "When beer or wine is examined by this method, the estimation of alcohol has a tendency to be too low." This is perfectly true when the usual formula is employed in the calculation, but it appears to be the formula, and not the process, which is principally at fault. The rule given is to divide the specific gravity of the original liquid ( $s$ ) by that of the "extract" ( $s'$ ), the assumption being that the difference between these two gravities is proportional to that between 1, the gravity of water, and the required gravity of the alcohol distilled away. Let us examine this assumption and see how far it tallies with the facts.

A given measure of an alcoholic liquid containing a fixed extractive, of which the gravity is known, is boiled until the whole of the alcohol is driven off; it is then made up to the original volume with distilled water, and the gravity again taken; it is clear that we have in the first case a certain quantity of fixed matter dissolved in a given bulk of dilute alcohol, in the second the same quantity of fixed matter dissolved in the same bulk of water; it would seem, therefore, that the difference between the two gravities should

be identical with, not proportional to, the difference between 1 and the required gravity, and this would be correctly represented by the formula  $1 - (s' - s)$ . The amended formula has the advantage not only of superior accuracy, but also of demanding much simpler arithmetical work than the old one. Where the gravities concerned lie near to unity, the difference between the results given by the two formulæ is unimportant, but where liquids of high gravity are under examination, such as sweet wines and liqueurs, the error may become serious. The following practical example will illustrate this: nine volumes of weak syrup were mixed with one volume of ordinary rectified spirit; the gravity of the mixture was 1.1228 (s).

A measured quantity was distilled with the proper precautions, and the distillate made up to bulk at the same temperature; the gravity was 0.988.

The residue in the retort was now made up to bulk as usual, and the gravity taken.

It was 1.1343 (s'), then  $\frac{1.1228}{1.1343} = \left(\frac{s}{s'}\right) = 0.9899$ ; and  $1 - (1.1343 - 1.1228) = (1 - (s' - s)) = 0.9885$ .

It will be seen that there is still a deficiency in indicated spirit-strength, and this is greater than I have usually met with in practice. I believe it to be due to the difficulty of concentrating a syrupy liquid without some slight decomposition; the residue in the retort was in fact slightly coloured. The quantity of extractive in ordinary wines and beers is of course much less than that used above, the object of the experiment being to emphasize the erroneous indications of the old formula.

#### DISCUSSION.

The President thereupon stated that Mr. Allen was unavoidably absent that evening and had requested him to give an abstract of the paper which Mr. Allen had intended to read, and which was the outcome of a conversation he had had with Mr. Blunt.

He (Mr. Hehner) had also made some experiments, to ascertain experimentally, which of the two formulæ for calculation was the correct one.

He prepared a dilute alcohol, the specific gravity of which, when 50 c.c., were, by the addition of water, made up to 100 c.c., was 0.9775. This alcohol, after distillation again, showed a specific gravity of 0.9775, showing that careful distillation did not entail any loss of alcohol whatever. He further made a sugar solution, 50 c.c., of which, when made up with water to 100 c.c., had a specific gravity of 1.0575. A mixture of 50 c.c. each of the alcohol and sugar solution, also made up to 100 c.c., had a specific gravity of 1.0356, determined twice on separate mixtures.

100 c.c. were then distilled, and both the distillate and the residue in the retort made up to 100 c.c. The gravities were determined, and found to be 0.97757 and 1.0577. Now, calculating by the division formula, the specific gravity of the spirit would be 0.9791, and by subtraction 0.9779, the former corresponding to 29.92 per cent of proof-spirit, the latter to 32.19 against 32.91 taken.

These figures, which were, as far as he (Mr. Hehner) could see, free from any source of error, absolutely confirmed the contention of Mr. Blunt, that the division formula was incorrect.

It was remarkable that this matter had escaped notice so long. In the work on Wine, written by Dr. Thudichum and their distinguished and respected past President, Dr. Dupre, the matter was discussed at some length; but, while the division formula was declared to be the correct one, it was stated that by the subtraction method the more accurate results were generally obtained. In quite a modern work, by Dr. J. Koenig (*Untersuchung landwirthschaftlich: wichtiger Stoffe*), the difficulty is got over by the bold declaration that the two formulæ were identical. This is, of course, not the case, as can readily be seen from an example. If a mixture of sugar solution and alcohol had a specific gravity before boiling of 1.2, and after boiling of 1.4, then the division formula would give 0.857, and the subtraction formula 0.800 as the gravity of the alcohol.

Mr. Bodmer said that he had not had the advantage of hearing the commencement of the paper, but that he had nevertheless gathered its meaning. He had recently had occasion to sample commercial spirits, and had generally found that the subtraction method was inaccurate; but when the amount of sugar present was not excessive then the division method and distillation method agreed very closely.

The President asked Mr. Bodmer how much sugar he had found in gin?

Mr. Bodmer replied that he had never determined the amount of sugar directly, but the gravity of the de-alcoholized gin was as much as 1.010, and, in extreme cases, 1.015.

Since the reading of Mr. Blunt's paper, my assistant, Mr. Skertchley, has, at my request, made the following determinations. A number of mixtures of alcohol, sugar and water were made. 100 c.c. were distilled, and the specific gravities of the original mixtures, and of the distillates, and of the residues in the retort were carefully taken in duplicate, after the fluids had been made up to 100 c.c., all measurements being made at 15.5°C.

| Specific gravity<br>of Mixture. | Sugar sol. | Distillate. | Division. | Subtraction. |
|---------------------------------|------------|-------------|-----------|--------------|
| 1.0036                          | 1.0175     | 0.9855      | 0.9863    | 0.9861       |
| 1.0211                          | 1.0468     | 0.9738      | 0.9754    | 0.9743       |
| 0.9831                          | 1.0254     | 0.9579      | 0.9587    | 0.9577       |
| 1.0504                          | 1.0626     | 0.9866      | 0.9885    | 0.9878       |

Thus, in all cases, the results obtained by subtraction are closer to those obtained by distillation than are those by Tabarie's formula, and the results are better the greater the alcoholic strength.

O. H.

The Secretary then read the following paper, also an extract from a letter received from the author,

### ON THE ADULTERATION OF WHITE PEPPER.

By W. F. K. Stock, F.C.S., F.I.C.

JUDGING from numerous papers to be found in THE ANALYST, the analysis of White Pepper has already often been a subject of enquiry, and much useful information has been afforded by former investigators. There are, however, certain facts connected with the sophistication of White Pepper which either have not attracted the attention of analysts, or which, if known, have not been made public; and it is with these facts that I shall deal in the present communication.

Some time ago a firm of retail dealers in this county was proceeded against for selling White Pepper containing 4 per cent. of added mineral matter, which proved to be a mixture of sulphate and carbonate of lime. The case was strongly defended, the wholesale merchants guaranteeing all cost. A conviction was obtained, and a fine of £2 was inflicted. The costs reached £34. Shortly after this the merchants wrote to me asking me to undertake the analysis of all their Peppers—White and Black—and it was arranged, at my suggestion, that the analysis should show the following items:—

Total Mineral Matter (Ash at low redness),  
 Sand in Ash,  
 Sulphate of Lime in Ash,  
 Carbonate of Lime in Ash,  
 Woody Fibre,  
 Microscopical Examination.

It was clear that nothing in the shape of adulteration could escape such a method of examination, and I shortly had an opportunity of proving its usefulness.

I received a parcel of 5 Samples of White Pepper upon which I was asked to report as to whether they were genuine. No information was given. The results of my analyses were as follows:—

| Nature of Determination.                             | No. 1  | No. 2  | No. 3  | No. 4  | No. 5  |
|--|--------|--------|--------|--------|--------|
| Total Mineral Matter (Ash) ... ..                    | 2.25 % | 9.90 % | 8.35 % | 5.55 % | 1.82 % |
| Sand in Ash ... ..                                   | trace  | .28 "  | .38 "  | .23 "  | .43 "  |
| Sulphate of Lime in Pepper ... ..                    | trace  | 2.85 " | .57 "  | 2.10 " | .12 "  |
| Carbonate of Lime in Pepper ... ..                   | .29 "  | 5.07 " | 5.59 " | 2.20 " | .27 "  |
| Woody Fibre ... ..                                   | 9.66 " | 9.73 " | 9.74 " | 3.66 " | 3.40 " |
| Microscopical Examination for Foreign Structures ... | none   | none   | none   | none   | none   |

I said of these samples :—

No. 1—Genuine White Pepper made from imperfectly \*decorticated corns.

No. 2—A bleached or doctored sample.

No. 3—A doctored sample.

No. 4—A doctored sample made from decorticated corns.

No. 5—A genuine sample of good quality.

As might have been expected, bold statements like the foregoing from a provincial analyst, who could not be supposed to know anything about either pepper or pepper grinding, did not fail to give rise to considerable correspondence. As one result, several lots of Pepper were sent back to the grinders. This firm at last addressed me personally, assured me that I was quite mistaken in my ideas about White Pepper, and offered to send me ground and unground genuine samples for my own analysis and information; at the same time they attributed the excessive ash in some samples to the process of "grading," by which I presume they meant the process of separating the ground pepper into its various qualities. I accepted the offer of the samples, and promised to communicate the results of my analyses to them on certain conditions, and the chief of them was that they should inform me *in what proportions the Pepper was "graded."* This (as I expected) they expressed themselves as quite unable to do.

However, for my own information and that of other analysts, I did proceed with the analyses of 14 samples which were duly sent me, and I obtained the following very singular and interesting results :—

FOUR SAMPLES OF WHOLE CORNS GROUND IN THE LABORATORY.

| Determination.            | Tellicherry. | Siam.   | Lampong. | Penang. |
|---------------------------|--------------|---------|----------|---------|
| Ash ... ..                | 1.05 %       | 1.45 %  | 2.20 %   | 2.75 %  |
| Fibre ... ..              | 4.86 "       | 4.43 "  | 4.90 "   | 5.06 "  |
| Calc. Carb. in Pepper...  | .58 "        | .62 "   | .81 "    | 1.67 "  |
| Calc. Carb. in Ash ... .. | 55.20 "      | 42.70 " | 36.80 "  | 60.70 " |

Four samples received in ground state, said to be same as above.

| Determination.               | Tellicherry. | Siam.   | Lampong. | Penang. |
|------------------------------|--------------|---------|----------|---------|
| Ash ... ..                   | 1.10 %       | 2.65 %  | 3.65 %   | 3.10 %  |
| Fibre ... ..                 | 4.10 "       | 4.93 "  | 6.60 "   | 6.16 "  |
| Calc. Carb. in Pepper ... .. | .54 "        | 1.88 "  | 2.43 "   | 2.20 "  |
| Calc. Carb. in Ash ... ..    | 49.00 "      | 71.00 " | 66.60 "  | 71.00 " |

\* By decorticated corns is meant those pepper corns which are imported for the purpose of producing White Pepper, and from which the true cortical layer of the berry has been removed by a rough process. There is a decorticated white known in the trade, but in this the inner layer corresponding to the liber of an exogenous stem has also been removed, and only the clean kernel remains.

*Six samples of Blended and Graded White Pepper also said to be produced from the above.*

| Determination.         | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. | No. 6.  |
|------------------------|--------|--------|--------|--------|--------|---------|
| Ash ... ..             | 1.47 % | 2.45 % | 3.05 % | 3.55 % | 4.90 % | 4.35 %  |
| Fibre ... ..           | 1.70 " | 3.33 " | 3.43 " | 4.00 " | 8.23 " | 10.43 " |
| Calc. Carb. in Pepper  | .69 "  | 1.61 " | 2.20 " | 2.50 " | 3.15 " | 2.16 "  |
| Calc. Carb. in Ash ... | 47.0 " | 66.0 " | 72.0 " | 70.4 " | 64.3 " | 49.6 "  |

In connection with these analyses, I may say that I was well aware of the practice of bleaching and facing white pepper corns, having got samples of both bleached and faced corns from well known houses; but I was hardly prepared for the great differences found in the percentage of ash and the percentage portion of lime to ash in *terms of carbonate* exhibited by these samples. The latter comparison is an idea which has proved of the greatest service in the analysis of White Pepper. I was quite satisfied, from the figures obtained, that the samples sent ready ground had received an addition of carbonate of lime, but in order to set the matter quite at rest, a flotation experiment with chloroform was made, and the carbonate of lime, *in the form of chalk*, was duly discovered and identified.

The analyses of the graded samples, in spite of the alleged increase of ash by grading, show that carbonate of lime has been added, but it was thought worth while to ascertain by experiment what foundation such an allegation could have in fact. To this end, two samples of Tellicherry Pepper were analysed; the one undecorticated, the other decorticated, when the following results were obtained:—

| Determination.  | Undecorticated. | Decorticated. |
|---|-----------------|---------------|
| Total Ash ... ..  | 4.02            | 1.64          |
| Fibre ... ..  | 10.40           | 6.80          |
| Percentage proportion of Lime to ash in<br>terms of Carbonate } | 27.30           | 62.00         |

These figures prove beyond doubt that the natural calcium compounds of Pepper are more abundant in the kernel than in the husk, and that instead of the calcium compounds augmenting directly as the proportion of husk, they are in inverse proportion. The analyses just given cannot be compared with analyses of *bleached* samples, because the calcium compounds and the fibre are profoundly affected by the bleaching process. In dealing with this question, we must keep the fact in view that by no process of grading can the normal relation of the ash constituents of the *kernels* be disturbed. This fact,

joined with a knowledge of the natural percentage of ash, and the normal relation of lime to ash in terms of carbonate, gives the necessary data for determining any abnormal proportion of calcium salts in white pepper.

I was assured by the grinders of these Peppers that analysts, members of this Society, were in the habit of passing, as genuine, ground White Pepper with 5 to 6 per cent. of ash. If this be true, the said analysts are not doing their duty. No genuine White Pepper, according to my experience, contains more than 2.75 per cent. of ash; and if grinders choose to bleach and face White Pepper, they must expect to share the fate of those who, a while ago, put a false complexion upon Tea. For myself, I shall pass no sample where the ash exceeds 3 per cent., and where I find the proportion of lime to ash, in terms of carbonate, to exceed 60 per cent. Whilst adopting these figures, I have no doubt they allow considerable latitude, for they are got from the analysis of Penang White, which is apparently lower in quality than any other White Pepper used. That the ash standard is quite fair for commercial samples is shown by the following table of analyses of 100 samples of White Pepper, collected indiscriminately by the Inspectors of Food and Drugs acting for the County of Durham:—

*Determinations of Total Ash on 100 Samples of White Pepper.*

| Between<br>1 % & 1.5 % | Between<br>1.50 % & 2.0 % | Between<br>2.0 % & 2.50 % | Between<br>2.50 % & 3.0 % | Between<br>3.0 % & 3.45 % |
|------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 26 Samples.            | 37 Samples.               | 18 Samples.               | 9 Samples.                | 10 Samples.               |
| Lowest Ash             | ...                       | ...                       | ...                       | 0.80 per cent.            |
| Highest „              | ...                       | ...                       | ...                       | 3.45 „                    |
| Average „              | ...                       | ...                       | ...                       | 1.914 „                   |

In conclusion, I feel that when an adulteration amounting apparently to only 2 per cent. is in question, the lay mind is apt to look upon the offence with considerable leniency; and, if it were only a question of bulk and weight, it would, comparatively, be of small importance. But there are two points which the analyst must always have clearly defined in his own mind. The first is, whether the article is, according to the best of his knowledge and belief, genuine. If not, he cannot truthfully pass it as such, no matter how small the proportion of adulterant used; and one has only to turn one's thoughts to the presence of alum in bread to see the force of this. Then he must have regard to the purpose for which the adulterant is used: and in the case of White Pepper—an article of which colour is a guiding feature of quality, there can be no doubt that chalk or other lime compound, when present, is used to produce fictitious whiteness.

The President, having invited discussion,

A Member enquired whether the sample referred to in Mr. Stock's letter was purchased from a wholesale firm, or from a retail dealer?

Mr. Bernard Dyer replied that he could add nothing to the information afforded by



Mr. Stock, which was, that the sample in question was purchased from "a well-known firm in the City of London."

Mr. Stokes remarked that anybody who tried to get the fibre out of pepper by the ordinary method of treating it with sulphuric acid and potash, was well aware, that on treating by potash one got a gelatinous mass which would not pass through a filter. He would like to know how Mr. Stock managed to make a separation.

Mr. Bernard Dyer said that he could not reply on the author's account, as he was not acquainted with the method followed by him. But he might tell Mr. Stokes, from his own experience, that he could avoid the trouble he had mentioned by extracting his pepper first with ether, and then with alcohol. The pepper, after being thus extracted, was treated with acid and alkali in the ordinary way. By following that course himself, he had altogether overcome the difficulty which Mr. Stokes mentioned, and the fibre could be filtered easily and quickly.

The President wished to draw the attention of the members to a very interesting paper on this subject, which had appeared in a recent number of *Zeitschrift f. angewandte Chemie*,\* and of which an abstract would appear in the ANALYST shortly. Mr. Stock appeared to doubt that genuine pepper could be graded; but he (the President) ventured to think that he would be of a different opinion if he had read the paper in question. For his own part he did not like a hard and fast line being drawn with reference to the amount of ash which white pepper should contain.

Mr. Stokes then read the following paper:—

### THE ESTIMATION OF FAT IN MILK.

By A. H. STOKES.

In the *Berichte*, vol. xxiv., p. 2204, there is described and figured by E. Molinari, an apparatus for rapidly estimating fat in milk. It is also described and illustrated in the last number of THE ANALYST. The apparatus is very delicate and, as figured, exceedingly difficult to clean. It is claimed that an analysis would take from 30 to 35 minutes, though if you sum up the times given by the inventor for each step of the process, it will take at least 50 minutes. But then, as a fat determination can, with only a simple tube, already be performed equally accurately in 20 minutes, there is no gain of rapidity. If it requires, as it probably would, half an hour besides to clean up the apparatus, there would be a great loss of time.

The idea of the apparatus is to prevent any transference from one vessel to another; the fat is set free, washed and weighed all in the same vessel.

I have devised a far simpler apparatus which will do this equally effectually.

It consists (see fig 1) of an Erlenmeyer flask of about 50 c.c. capacity, to the neck

\* See abstract in this Journal, page 235.

of which is joined a bulb of about 60 c.c. capacity terminating at the apex in a short glass tube with a tap to it. At the neck, where the bulb joins the flask, is a short side tube which can be closed by a cork. It is used thus:—

After being weighed, 10 grammes or 10 c.c. of milk are placed in the flask, heated almost to boiling, and about 10 c.c. of strong HCl added, this mixture is boiled over a flame for about one minute, left hot for about three minutes, then cooled down and ether poured in nearly up to the neck. The tap is closed, the cork inserted and the apparatus well shaken and then left for about five minutes to rest with the tap end downwards. The tap is now opened and as much as possible of the acid liquid allowed to run out. The tap is closed, the cork taken out and about 10 c.c. of water run in and shaken with the ether and allowed to run out again through the tap; after standing awhile a second quantity of water is thus used.

Finally, the tap is closed, the side tube connected to a condenser, the ether distilled

off, and the apparatus with its residual fat placed in the water-bath to dry. This drying, I find, takes a very long time.

The apparatus is very simple. The fat never leaves the apparatus after the milk is put into it but is treated and weighed all in the same vessel; no calculation is required. The objections to it are the difficulty of running off the acid or aqueous fluid so close as to leave none in the flask, or, on the other hand, to let none of the



Fig. 1.

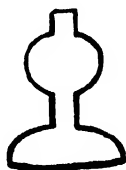


Fig. 2.

Fig. 3.



ethereal solution escape; the flask, being wet inside with water, takes a long time, sometimes hours, drying.

A simpler and quicker process is the use of another piece of apparatus (fig. 2), in which a 25 c.c. flask, having a neck of  $\frac{3}{4}$ -inch diameter and one inch long, is surmounted by another flask of about 35 c.c. capacity, terminating with a mouth of  $\frac{3}{4}$ -inch diameter. Into this 10 grammes or 10 c.c. of milk are placed; it is then heated on the water-bath, directly the milk is near  $100^{\circ}$  C. the HCl is poured up to a mark near the beginning of the neck. By thus heating the milk before adding acid, no clots of curd are formed. After boiling for about one minute and leaving it hot for three minutes, it is cooled by placing it in a basin of water; the shape of the apparatus makes it float easily, so that there is no danger of its being immersed, however deep the water may be. It is now filled with ether up to about the middle of the upper bulb, a cork is inserted in the mouth and the whole violently shaken. On letting it stand about three minutes it will be found that the brown acid liquid comes up to the middle of the neck with a very slight layer of fluffy white casein between it and the ether.

Taking out the cork, a double tube arrangement like that of the ordinary wash-bottle is inserted. The cork of this should not be of indiarubber, but of ordinary cork, for two reasons: first, because a glass tube does not slide easily in rubber exposed to ether

vapour; second, to avoid any chance of a solution of rubber being weighed off as fat. The longer tube of this is forced down till it almost touches the casein layer. A weighed flask is placed under the upper end of the tube, and by blowing into the other tube the fat-ether solution is driven into the weighed flask. About 10 c.c. more ether is placed in the apparatus and the whole shaken; after three minutes settling this ether is added to the first quantity. Another repetition of this leaves the liquid practically free from fat. The weighed flask is connected to a condenser and the ether distilled off. I find that if the flask is almost entirely immersed in boiling water, the ether does not boil violently, but is rapidly and quietly distilled off.

In fact, it will evaporate as quickly as if placed in an open dish on the water-bath. The flask is now dried in the air-bath for fifteen minutes and then weighed. The weight of fat multiplied by 10 gives the percentage if 10 grammes of milk were taken. If 10 c.c. were taken it is only necessary to divide the weight of fat by the specific gravity of the milk. In about 30 minutes the whole process may be completed.

With both pieces of apparatus I have obtained results identical with the calculated results and with those of the paper-coil process. In both cases the acid liquid and the washings are put into residue bottles and the ether afterwards recovered, so that hardly any ether is lost.

The principles of these are just the reverse of one another; from one the acid solution is expelled, from the other the ethereal solution is expelled. Apparatus No. 2 is by far the quicker, easier and less liable to error. It embodies Mr. A. H. Allen's principle of doing away with calculation; the narrow neck in the middle enables the ether to be drawn off almost entirely each time; the shortness of the bulb containing the ether allows the acid to settle out in the quickest possible time after shaking.

But neither of these methods is so rapid as the use of the long tube described in ANALYST XVI., p. 71, a figure of which I show to-night (fig. 3) alongside of the original short tube. By the use of a centrifugal apparatus giving about 3,000 revolutions per minute, I can separate in this the ethereal layer in one minute, and, working in the way described in the *Chemical News*, of November 1st, 1889, can complete a fat extraction in 15 minutes; without the centrifugal apparatus the fat has been frequently determined in 20 minutes accurately in my laboratory.

Before trying any special apparatus, I experimented to see if there could be any destruction or loss of fat. I boiled known weights of butter-fat with HCl and water, extracted with ether, and recovered exactly the same amount of fat I put in, unaltered. I took quantities of the brown acid liquid after it was done with, and found it to be absolutely free from any fat. The fat obtained in the other cases I have examined and found to be nothing else but butter-fat.

I experimented with ether containing known percentages of alcohol; up to  $1\frac{1}{2}$  per cent. alcohol does not interfere with the process.

Ether containing fat can be blown off or pipetted off just as easily as water. I tried other solvents than ether and other acids than HCl.

Occasionally on boiling milk with  $\text{HCl}$  and shaking it with ether, it forms a gelatinous mass from which the ether will not readily separate. This is usually due to not having boiled the two together long enough. On the other hand, too long boiling causes the casein to form bulky black flakes. The boiling may safely last from one to three minutes. If a milk does not turn the usual dark brown colour after three minutes you may be sure it has been watered.

After a practical experience of every known method of fat extraction of milk, and a three years' special devotion to this method, I can assure the Society that there is no other method that at present can possibly compare with it for accuracy, simplicity, rapidity and cheapness, whether applied to cream, whole milk, skim milk, sour milk or condensed milk (sweetened or unsweetened).

No analyst of my acquaintance after trying this method has gone back to any other, and I know now some dozen who habitually practise it.

To my assistant, Mr. W. N. Yarrow, I am indebted for the diagrams shown to-night.

I am pleased to bear testimony to the wonderful way in which fats thus determined agree with the calculated results given in the admirable table of Messrs. Hehner and Richmond in *THE ANALYST*, XIII., p. 26.

#### DISCUSSION.

Mr. Cassal said that while the special object of Mr. Stokes' paper was not quite clear, all would, no doubt, agree, that the Werner Schmid process was very valuable. The minute description of the pieces of apparatus represented by the diagrams appeared to be hardly necessary. The apparatus, described at such length by Mr. Stokes, seemed to be ingenious, but then Mr. Stokes had said that it should not be employed, as it was no use, and that it was almost impossible to clean it and dry it. He submitted, therefore, that this apparatus would not commend itself to the members of the Society. Mr. Stokes had described another piece of apparatus, which closely resembled a wash bottle. Mr. Stokes stated that he originally used a straight tube, of which an illustration was before them. A highly satisfactory point about the Werner Schmid process as amended, was, that after extracting with ether, one could blow out the whole of the ethereal solution by means of the apparatus suggested by Mr. Chattaway, evaporate it, and weigh the total amount of fat. The removal of a measured portion of the solution, by the reading off of the residual portion, was very undesirable in such a process, and formed a source of error. When, without unduly increasing the time legitimately required for such operations, one could obtain and weigh the *whole* of the fat in the portion of milk taken for analysis, he did not think that there was any advantage to be gained by the measurement modification sufficient to compensate for the risk. He himself had found that excellent results could be obtained by the Werner-Schmid process, and Mr. Stokes was to be thanked for having introduced it to their notice. He (Mr. Cassal) had found that accurate results were most satisfactorily obtained

by the use of a simple tube provided with the wash-bottle arrangement, suggested by Mr. Chattaway, and which he had just referred to. Mr. Cassal wished to state that his approval of the Werner Schmid process was mainly based upon its value for the analysis of decomposed milk. If a large number of analyses of fresh milk had to be done, and something else at the same time, the Adams process should be adhered to, for the simple reason that it would go on automatically. That, however, did not detract from the superior value of the Werner Schmid process when employed under specific circumstances.

Mr. Bernard Dyer thought that Mr. Cassal had, he was sure unintentionally, hardly treated Mr. Stokes quite fairly, though he (Mr. Dyer) agreed with Mr. Cassal that it would have been perhaps better that they should not have been troubled with a lengthy description of an apparatus which they were afterwards advised not to use. One of the features of the Schmid process was that one need not trouble to take off all the ether, but could stop it at any graduated point which one might think desirable. Mr. Cassal, however, had said that he did not consider that fractional removal was a good method of working, but that it was much better to take off the whole of the ether at one operation. Now it seemed to him that Mr. Stokes had devised a simple substitute for the original Schmid tube, by means of which he did take off the whole of his ether, thus doing exactly what Mr. Cassal would do with the original tube, on which he had the graduations, but thought it unnecessary to make use of them. If he remembered rightly, Mr. Stokes had told them on previous occasions that the method of pipetting and not troubling to remove the whole of the ether gave results which were very satisfactory indeed.

The President asked Mr. Stokes to state what was the number of analyses which he considered a man could conscientiously and honestly make in a day by means of the process before them.

Mr. Stokes replied that he considered the advantage to be this: that whereas it was impossible by the old process to analyse a sample in half-an-hour, it could easily be done by the method which he had brought forward.

The President said, that he looked upon methods which were said to give results in such a short time, with the greatest suspicion. Fat could not well be dried in an extraction-flask under a quarter of an hour, and the flask itself would have to stand before it could be accurately weighed for about 10 minutes, which almost made up the half-hour given by Mr. Stokes. He could see no possible object or advantage in these rapid analyses. They were all obliged to Mr. Stokes for bringing the Werner Schmid process so prominently before them, and for proving that it was capable of giving good results. Yet, having heard all that had been urged in favour of the process, he (Mr. Hehner) could yet not see where its advantage over the excellent Adams method lay. That process was absolutely automatic, and required the least possible amount of attention, which was a more important point for the analyst than extreme rapidity. He was of opinion that it would be far better for public analysts to stick to the Adams process, which had been universally accepted as being the most accurate one,

unless any other process effected a decided improvement upon it. For his own part, he could not see that the method so strongly recommended by Mr. Stokes possessed such decided advantage.

Mr. Cassal said that he had stated that the tube, which formed part of Mr. Stokes' wash-bottle apparatus, was originally suggested by Mr. Chattaway, but he understood Mr. Stokes to say that that was not correct. He therefore thought it necessary to ask Mr. Stokes to explain to the meeting the precise difference between the two forms of apparatus. His own impression was, that at the time the Werner Schmid process was first introduced to their notice, the use of an ordinary tube—not graduated or narrowed—was recommended by a member present, and that then Mr. Chattaway explained that he had devised a modification of the wash-bottle for the purpose of removing the whole of the ethereal solution after the treatment of the milk.

Mr. Stokes, in reply, said the main reason for the modifications which he had introduced was that he required to make his determinations quickly. If he had to wait for every operation he would lose a lot of valuable time, which he could not afford. That brought him to the President's question, namely, how many could a man honestly do in a day? He was hardly in a position to give a definite reply to that question, as he had never had occasion to do fat determination only; but he might say that he had 30 or 40 samples to test in a day, and they had to be done promptly. Mr. Dyer had suggested the excision of what he called the intermediate apparatus. The diagram ("ANALYST" xvi. 209) had already been given in the Journal of their Society, and he conceived that a man on first seeing it might consider it to be a good idea, as it really looked so theoretically, and waste time in trying to work it. In order to avoid that, he had shown a simpler apparatus that answered the same purpose could be made for the small sum of 2s., and which would be of use for other purposes than extracting fat from milk. Coming to Mr. Cassal, that gentleman had said that he found a great advantage in blowing off the whole of the ether. He (Mr. Stokes) quite agreed with him, but if Mr. Cassal meant to inform him that ether shaken up with the acid fluid would separate as rapidly in the long tube he had hitherto employed as it would in the short bulbs now before the meeting, he would be surprised indeed. For his own part, he believed that some day Mr. Cassal would adopt the apparatus which he had brought forward, and would admit that it had advantages over any hitherto employed for the purpose.

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The following "Notes from the Khedivial Laboratory," by H. Droop Richmond, were taken as read:—

1. The relation between Specific Gravity, Fat, and Solids not fat in the milk of the Gamoose.
2. The estimation of Iodoform.
3. The testing of Petroleum.

This terminated the proceedings of the Society.

**Rapid valuation of Commercial peptones.** By M. A. Denaeyer. (*Journal de Pharmacie Anvers. Novembre, 1891*).—Alcohol of 95% added in excess to concentrated solutions of meat peptone precipitates undigested *albumins*, *albumoses*, *pure peptone* and *gelatin*. On the other hand the alcohol separates by solution:—

(1.) The extractive principles of meat (*carnine*, *creatines*, *creatinines*, &c.); (2) the products of decomposition of albumins (*leucine*, *tyrosine*, *aspartic acid*, &c.); (3) the products of decomposition of gelatins (*alanine*, *glycocoll*, *amido-butyric acid*, &c.).

It follows from these facts that alcohol constitutes an excellent agent for the valuation of commercial peptones; the larger the amount of the precipitate the greater will be the strength of the peptone in the nutritive elements; albumoses, peptone, acid-albumins.

We must remember that albumoses and true peptone are only found in peptones produced by the digestion by means of gastric juice; the acid-albumins which enter into the composition of artificial peptones (*vapeur peptones*?) have apparently, as far as assimilation is concerned, no higher value than ordinary albumin.

The determination in a peptone of the matters soluble in alcohol is made by dissolving 2 grms. of peptone, calculated as dry matter, in about 10 c.c. of water. This solution is precipitated by 100 grms. of alcohol, and the mixture is allowed to stand for 24 hours in a cool place. The alcoholic solution becomes quite clear; it is decanted, and the precipitate washed, the alcohol distilled off and the residue evaporated to dryness in a basin on a water bath. The desiccation is completed in an oven at 105° C. to constant weight.

In the same way the weight of the alcoholic precipitate is taken after complete drying.

A well-prepared meat peptone should not give above 30 per cent. of alcoholic extract, but commercial preparations are found which yield as much as 60 per cent. These extracts then contain besides creatines and normal extractive bases, great quantities of the products of decomposition of the albumins (*leucine*, *tyrosine*, *aspartic acid*, *caproic acid*, &c.), and of the gelatins (*glycocoll*, *leucine*, *alanine*, *amido-butyric acid*, &c.) of muscular tissue.

In fact a few drops of the alcoholic solution evaporated on a glass slide show under the microscope leucine and tyrosine with their characteristic forms, besides other things.

These excrementitial products, destitute of alimentary value and formed in defective digestions at the expense of the albuminoids and colloids of meat, represent the deficiency in gelatin, albumin and peptone of these preparations.

The estimation of the alcoholic extracts allows, as will be understood from the above, of the determination of the dietetic equivalent of all preparations of meat peptone: it gives at the same time valuable indications as to the nature of the digestive operations.

It will be remarked that in very acid and long sustained digestions the alcoholic extract of the peptone obtained will be rich in the products of decomposition, whilst the

concentrated solution of peptone ( $\frac{2}{3}$ ) will only yield a small precipitate with the alcohol (30 to 40 per cent. at most).

On the contrary, in digestions faintly acid and well regulated in regard to duration, temperature, weight of pepsine, hydrochloric medium, &c., the alcoholic extract which the peptone yields will be small, but on the other hand the precipitate of gelatin, albumoses, and peptone very abundant (rising to 70 per cent.).

These assays are very interesting; we recommend them to our *confrères*. By a simple precipitation with alcohol they will be enlightened as to the respective merits of the preparations of peptone which they purchase.

C. W. II.

**On the Grading of Pepper.** By H. Trillich. (*Zeit., f. angew. Chem.* 1891, p. 516).—The Society of Bavarian Chemists having resolved that the highest permissible limit of ash in black pepper be 5.6, with 2 per cent. of matter insoluble in acid, the author investigated the influence of milling and sifting upon pepper. The mill employed consisted of two grooved steel rollers. The crushed pepper passes on to a sieve, the siftings being separately collected, whilst the coarser particles went back upon the rollers over and over again, until no more would pass through the sieve. The remainder went into another mill, and was sifted once more. Thus 12 different siftings were obtained, which were separately examined. The first and second portions showed a fairly equal mixture of black particles of husk and white particles of the inner berry. The subsequent products become successively lighter up to a certain point, and then again darker until the last consist of greyish black particles, mostly consisting of husk.

The first series of experiments were made with Prima Singapore pepper, the berries containing 3.54 per cent. of ash with 0.09 per cent. of sand. 1,000 grammes contained 0.275 grammes of dust, with 0.08 grammes ash (29%), and 49.80 grammes of stalks, with 0.655 ash (13.1%). 1,250 kilos were ground, and the separate portions gave the following results:—

| No. | kilo. | Weight.<br>p.c. | Water. | Ash. | Sand. | Pure Ash. |
|-----|-------|-----------------|--------|------|-------|-----------|
| 1.  | 284   | 22.7            | 13.89  | 3.71 | 0.37  | 3.34      |
| 2.  | 209   | 16.9            | 14.10  | 2.86 | 0.15  | 2.71      |
| 3.  |       |                 | 14.22  | 3.04 | 0.27  | 2.97      |
| 4.  |       |                 | 13.49  | 3.17 | 0.19  | 2.98      |
| 5.  | 338   | 27.1            | 13.16  | 3.30 | 0.17  | 3.13      |
| 6.  |       |                 | 13.34  | 3.50 | 0.16  | 3.34      |
| 7.  |       |                 | 12.96  | 3.80 | 0.13  | 3.67      |
| 8.  | 198   | 15.8            | 13.10  | 3.82 | 0.15  | 3.67      |
| 9.  |       |                 | 12.87  | 3.95 | 0.10  | 3.85      |
| 10. |       |                 | 12.89  | 5.11 | 0.13  | 4.98      |
| 11. | 218   | 17.5            | 12.38  | 7.52 | 0.09  | 7.43      |
| 12. |       |                 | 12.91  | 7.50 | 0.10  | 7.40      |



The greater portion of the sand, therefore, goes into the first part of the product, the percentage of ash in which is large. Curiously, the amount of ash in the following portions steadily increases, while the sand remains practically the same, but the last two fractions have a much higher amount of ash with still less sand.

The second series of analyses were made upon products similarly obtained with Lampong pepper, which is of lower quality than Singapore. The berries contained 4.50 per cent. of ash with 0.52 per cent. of sand. 1,000 grammes contained 6.004 grammes dust, with 2.704 ash, or 45.03 per cent., and 1.957 grammes sand, or 32.58 per cent.; also 1.691 grammes woody pepper portion, with 0.256 ash or 15.14 per cent.; 0.111 sand, or 6.56 per cent., and 4.877 grammes stones. These impurities would raise the percentage of ash and of sand in the pepper to, as near as can be estimated, 5.60 per cent. and 1.50 per cent. respectively.

The following are the analyses of the various fractions:—

| No. | Weight. |      | Water. | Ash.  | Sand. | Pure Ash. |
|-----|---------|------|--------|-------|-------|-----------|
|     | kilo.   | p.c. |        |       |       |           |
| 1.  | 72.5    | 13.8 | 12.72  | 10.92 | 5.66  | 5.26      |
| 2.  | 49.5    | 9.4  | 12.82  | 6.98  | 2.86  | 4.12      |
| 3.  | 54.0    | 10.3 | 12.99  | 6.30  | 1.93  | 4.37      |
| 4.  | 63.0    | 12.1 | 13.37  | 5.82  | 1.22  | 4.60      |
| 5.  | 54.0    | 10.3 | 12.98  | 5.24  | 0.71  | 4.53      |
| 6.  | 52.5    | 10.1 | 13.33  | 5.56  | 0.75  | 4.81      |
| 7.  | 30      | 5.7  | 13.29  | 5.18  | 0.51  | 4.67      |
| 8.  | 42      | 8.0  | 13.54  | 5.54  | 0.64  | 4.90      |
| 9.  | 43      | 8.3  | 13.70  | 4.91  | 0.28  | 4.63      |
| 10. | 35.5    | 6.8  | 13.18  | 5.67  | 0.35  | 5.32      |
| 11. | 13.5    | 2.6  | 11.72  | 7.46  | 0.43  | 7.03      |
| 12. | 13.5    | 2.6  | 11.94  | 7.22  | 0.46  | 6.76      |

Here again the larger fraction of the sand went into the first fraction, whilst the ash proper steadily rose.

O. II.

**The Adulteration of Basic Slag. Morgen.** (*Read at the 64th meeting of the Deutsch. Naturforsch. u. Aerzte. Through Chem. Zeit.*)—The adulteration of basic slag with aluminium phosphate can be detected by the loss on ignition, which, when it amounts to  $1\frac{1}{2}$  per cent. is an almost certain indication of falsification. The addition of Redonda phosphate is detectable by the determination of the specific gravity; the author prefers to use bromoform for this purpose, rather than the potassium-mercuric iodide solution employed by Loges. Besides these tests, the production of a copious precipitate with caustic soda solution is an indication of the presence of the same adulterant. The best method for the quantitative examination of basic slag consists in treating the sample with a 5 per cent.

solution of citric acid, in which the phosphoric acid natural to the slag is completely soluble while that of Redonda phosphate is not dissolved.

Faffin slag behaves similarly to Thomas slag, save that it remains suspended in bromoform. A new adulterant has been noticed by Loges, containing 4 per cent. of caustic lime, 6.4 per cent. of carbonate of lime, and the remainder calcium fluoride; it is said to be of English origin.

B. B.

[NOTE BY ABTRACTOR.—A letter appears in the *Chem. Zeit.* 1891, 1449, signed Warth and Wagner, pointing out that the loss on ignition is not to be relied on for detecting the adulteration of basic slag, as samples that have been exposed to air and moisture may absorb a good deal of water and carbonic acid, which they lose on ignition. An error in the contrary direction is imported by the circumstance that the slag may contain ferrous and manganous oxides and absorb oxygen on heating. The presence of calcium fluoride is not necessarily evidence of adulteration, as it may have been introduced for metallurgical reasons.]

**The sensitiveness of various Tests for Arsenic. C. O. Curtmann.** (*Pharm. Rundsch.* 1891., ix. 175. *Through Chem. Zeit.*)—The author has examined a number of tests for arsenic as to sensitiveness, and records the following results:—

1. Sulphuretted hydrogen; 0.01 mg.  $As_4O_6$  in 1 c.c. of liquid, gave a slight yellow turbidity after two minutes; 0.001 mg.  $As_4O_6$  gave a yellowish tinge after 15 minutes; when the dilution was greater no reaction was obtained.
2. Silver nitrate; 0.01 mg.  $As_4O_6$  in 1 c.c. gave a slight yellow turbidity after six minutes; the reaction ceased on further dilution.
3. Scheele's reaction; [Ammonium-Copper Sulphate]; 0.1 mg.  $As_4O_6$  in 1 c.c. gave a slight green precipitate immediately; the limit was reached with 0.01 mg., which gave a scarcely perceptible turbidity after some time.
4. Bettendorff's method [Stannous chloride in concentrated hydrochloric acid]; 0.1 mg.  $As_4O_6$  in 1 c.c. gave a slight brown colouration; 0.01 mg. gave no reaction.
5. Gutzeit's reaction [Action of arsenical hydrogen upon a very concentrated solution of silver nitrate]; 0.001 mg.  $As_4O_6$  in 1 c.c. gave a yellow stain after 30 minutes, which, when moistened, became bright brown. The limit was reached at 0.0001 mg. which gave a barely perceptible stain after one hour, the colouration becoming more perceptible on moistening and again drying.

It is therefore possible, by means of Gutzeit's reaction, to detect one part of arsenious anhydride in 10 million parts of solution. The method is, therefore, eminently suitable for testing reagents for analysis, but is far too sensitive for testing pharmaceutical preparations, for which purpose Bettendorff's method is better fitted.

B. B.

**On the estimation of Mixtures of Saponifiable and Unsaponifiable Fats.** M. Hönig and G. Spitz. (*Zeit. f. angewandt. Chemie.* 1891, p. 565).—The absence of concordant results in analyses of mixtures of the above-mentioned substances made by different chemists, may be traced to the inexactitude of the methods employed. These (putting on one side the iodine and bromine addition processes as entirely useless) are the three following:—

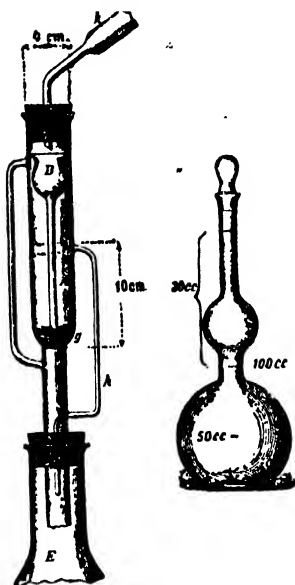
1. The mixture is saponified with alcoholic potash, the unsaponified portion being caused to separate either by boiling, or by being kept warm for some time. The separation is never complete, and, consequently, the results are always too low.

2. The soluble soap obtained by saponification with alcoholic potash is either as such, or after conversion into an insoluble soap, thoroughly dried and exhausted with ether or petroleum ether. This process only gives exact results when the soap is absolutely dry, and when the slight solubility of soap in petroleum ether is taken into account. Since the drying and extraction of the soap are both tedious operations, the process cannot be recommended for practical use.

3. The alcoholic solution of soap, obtained on saponification, is repeatedly shaken out with petroleum ether, or extracted in a suitable apparatus. This method, as shown by Morawsky and Dembsky (*Dinglers Polytechn.* 1885, p. 39), gives rigidly accurate results when certain precautions are taken. Messrs. Hönig and Spitz propose a modification which, without interfering with the exactness of the process, considerably shortens the time of its execution. This consists in using, instead of water, 50 per cent. alcohol for washing the petroleum ether layer, to remove the small quantity of soap taken up by it. By this means the two layers of fluid separate almost immediately. The two processes recommended are as follows:—

(A.) 7 to 10 grms. of the fat are boiled under a reflux condenser, with 20 to 25 c.c. of strong alcoholic potash and as much alcohol for 5 to 10 minutes; 30 to 40 c.c. of water added, and the whole boiled up once. After cooling, the soap solution is run into a separatory funnel, the flask rinsed out with 50 c.c. of alcohol, then with 50 c.c. petroleum ether, and the whole thoroughly well shaken. The alcoholic soapy layer quickly subsides, and is run off. The petroleum ether layer is now shaken out 2 or 3 times with 10 to 15 c.c. of 50 per cent. alcohol, the washings being added to the original alcoholic soap solution. The petroleum ether is emptied into a tared flask. The alcoholic soap solution is shaken out with repeated quantities of petroleum ether, until a drop of the latter leaves no fatty stain after evaporation on paper. The dissolved soap is removed from each of the petroleum ether washings by being shaken out thrice with 50 per cent. alcohol. The united petroleum ether washings are distilled off, a small weighed piece of pumice stone being added to prevent bumping. The last portions of petroleum ether are removed by heating the flask, and blowing into it. Petroleum ether boiling between 50 and 70° C. should be used. The alcoholic soap solution may, after boiling off the alcohol, be used for the estimation of the saponifiable fats by the usual methods. The whole process can be performed in an hour.

(B.) When many determinations have to be made at one time, the authors propose a



method of continuous extraction of the soap solution instead of shaking out, using for this purpose the modified form of a Soxhlet extracting apparatus shown in the accompanying illustration. Instead of the syphon, a small tube (*h*) is inserted about half way down the container *A*, and after one right-angled bend, passes downwards and enters the lower tube attached to the evaporating flask. A small thistle-headed funnel of such a length that its head is a short distance below the cork of the container, is inserted, its lower end dipping into a layer of glass beads about 1 centimeter deep. The alcoholic soap solution which, after dilution with water, should amount to about 50 c.c., is shaken up in the flask with about 20 c.c. petroleum ether, poured into the extracting apparatus, the flask again washed out with petroleum ether, and finally with 50 per cent. alcohol. The surface of the soap solution should be about half a centimeter below the mouth of the draining off tube.

After connection with the extraction flask, the small funnel is inserted, and 20 c.c. petroleum ether carefully poured in, the apparatus connected with a reflux condenser, and the ether kept boiling until it runs off quite colourless, and the soap solution is perfectly clear. The ether gradually becomes turbid from the soap dissolved; this must be removed by shaking out the solution several times with 50 per cent. alcohol in a separatory funnel.

(C.) If an approximate estimation only be required, the operation may be simplified as follows:—The saponification is effected in the flask shown in the figure, and which contains about 100 c.c. to the mark in the middle neck, this space being divided into two by a mark in the bulb. The amount contained between the marks in the upper and lower necks is exactly 30 c.c.; 2 to 3 grms. of the fat are saponified with alcoholic potash, after cooling, filled up to the 50 c.c. mark with alcohol, then made up to 100 c.c. with water, 30 c.c. petroleum ether added, and the whole repeatedly shaken. After perfect separation of the ether, 20 c.c. of it are pipetted off, placed in a tared flask, the ether driven off, the fat weighed, and the requisite calculation made. This method, as shown by examples, gives results to within 1 per cent. of the truth.

For the estimation of water, which, with the assistance of ammonia or ammonium carbonate, may be incorporated into the oil to the extent of 30 per cent., without being detected by superficial observation, the authors recommend 20 grms. of the well-mixed sample to be dissolved in about 100 c.c. petroleum ether, and allowed to stand for an hour, filtered through a tared filter into a tared flask, taking care no water reaches the filter. The residue and filter are washed several times with petroleum ether, the

ether driven off from the flask and filter, and the two weighed. The purified fat thus left may be advantageously used for analysis.

The water may be also estimated by dissolving 15 to 20 grms. of the fat in petroleum ether, placing the liquid in a burette filled up to the lowest mark with water, and after standing some time, directly reading off the water. The dregs are estimated by filtering the solution through a tared filter, washing with petroleum ether, drying and weighing.

W. J. S.

**The Determination of Earthnut Oil in Olive Oil.** Holde (*Mitt. König. Tech. Versuchs.*, 1891, 9, 105, through *Chem. Zeit.*).—The usual method of detecting and determining arachis or earthnut oil in olive oil, depending upon the isolation of arachidic acid needs modification in the case of oils containing only 5—10 per cent. of arachis oil, 40 grms. of the suspected oil being taken instead of the 10 grms. ordinarily prescribed. Moreover the arachidic acid isolated by extraction of the palmitic acid which accompanies it when the lead salts insoluble in ether are decomposed by hydrochloric acid must be repeatedly recrystallized from 90 per cent. alcohol until its melting point ceases to rise, unless it be over 70° C. at the first trial.

B. B.

**Adulteration of Dried Mushrooms.** P. E. Alessandri (*Zeits. Nahrungsmittel-Untersuchung u. Hygiene*, 1891, 5, 79, through *Chem. Zeit.*).—The author found in samples of dried mushrooms offered for sale, about 30 per cent. of unequally thick white discs, puckered or crumpled in aspect and brownish yellow (not chestnut brown) at the edges, which showed no wrinkles, hollows, or wavy lines like those on true mushrooms. They were coloured blue by iodine and when examined microscopically appeared to be simply pieces of turnip, dried discs of which presented the same appearance and behaviour.

B. B.

**Remedy for "Bumping."** E. Pieszezek (*Chem. Zeit.* 1891, 15, p. 1126).—The plan advocated consists in placing a glass tube about 5—8 cm. in length, and 5—10 mm. in width (the exact dimensions depending upon the bulk of liquid to be boiled) and closed at the upper end, resting against the side of the flask or other vessel to be heated, so that it stands nearly vertical with its open sharp-edged end pointing downwards. Boiling goes on quietly when once started, the bubbles making their appearance at the lower end of the tube. On cooling, the liquid rises in the tube which must therefore be raised and allowed to again become full of air before beginning the boiling again. The tube is best provided with a hook of platinum wire fixed in the upper end for ease of handling. The device is said to be efficient even for liquids containing heavy precipitates such as barium sulphate, and lead sulphate, and is also recommended for the Reichart-Vollny process.

B. B.

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# THE ANALYST.

JANUARY, 1892.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS

A MEETING of the Society of Public Analysts was held on the 2nd December, 1891, the President being in the chair.

The minutes of the last meeting were read and confirmed.

The following gentlemen were duly proposed :—

As members :—Dr. Samuel Rideal and Mr. James Nimmo.

As associates :—Messrs. Charles M. Caines and W. P. Skertchley.

Dr. William Robert Smith was duly elected a member, and Mr. E. H. Roberts an associate of the Society.

On the motion of Mr. Harvey, seconded by Mr. Woosnam, Messrs. Harland & Coste were elected Auditors for the year.

The following paper was then read by the author :—

### NOTE ON TABARIE'S PROCESS FOR THE INDIRECT ESTIMATION OF ALCOHOL IN BEERS.

By SYDNEY HARVEY.

THE alleged discrepancy between the indirect and the distillation methods for the estimation of alcohol in beers has for some time engaged my attention, and I have been trying to determine the amount of difference between the results yielded by the respective processes, and, if possible, arrive at the cause.

The following investigation was conducted upon four series of sound new beers with a minimum of acidity; and the plan adopted in every case was uniformly as follows :—

The samples were well shaken to expel as much as possible the carbonic acid gas; 200 c.c., exactly measured; slightly diluted with water and subjected to distillation, nearly 150 c.c. being drawn over. This distillate was made up to 200 c.c., as was the "extract" left in the retort; the densities of both these and also that of the original beer being carefully taken. The results were as follows :—

*Average Specific Gravities at 60° F. from 4 sets of Beers analysed. .*

|    | Beer.   | Extract. | Alcohol<br>Calculate L.<br>1—(E—B) | Alcohol by<br>Distillation. | Difference.                      |
|----|---------|----------|------------------------------------|-----------------------------|----------------------------------|
| 1. | 1·01131 | 1·01934  | 0·99197                            | 0·99167                     | 0·00030                          |
| 2. | 1·00826 | 1·01653  | 0·99173                            | 0·99119                     | 0·00054                          |
| 3. | 1·01608 | 1·02435  | 0·99173                            | 0·99137                     | 0·00036                          |
| 4. | 1·01971 | 1·02739  | 0·99232                            | 0·99189                     | 0·00043                          |
|    |         |          |                                    |                             | Average<br>Difference<br>0·00041 |

Referring to the above, the distillation process will in every case be found to yield an alcohol of lower density than by Tabarie's method; and this has been my constant experience. I think this somewhat remarkable, because at first sight one would suppose that the reverse would be the case, owing to *possible* loss of alcohol during evaporation and subsequent condensation.

That experiments conducted upon solutions of alcohol, pure sugar and water, when treated as above *do* yield identical results by either process, has, I think, been fully proved when the subtraction formula is applied.

The case of a complex fluid like beer, however, is not a parallel one, owing to the presence of carbonic acid—present in the beer, but absent in the “extract.” Clearly these two liquids to be strictly comparable should differ but in one respect, viz., the presence or absence of alcohol only.

The four series of beers above referred to were carefully examined for residuary carbonic acid, with the result that a pretty constant amount was found, averaging 0·1 gramme of CO<sub>2</sub> per 100 c.c., and never much under that quantity.

Before, however, claiming this carbonic acid as a factor in raising the density sufficiently, its effect upon water had to be ascertained, and as I could not find any published matter on this question, I resolved to investigate the subject myself. I charged distilled water with washed carbonic acid gas, and after numerous failures, owing to the troublesome disengagement of bubbles of gas in the specific gravity flasks, I at length arrived at the following results:—

*Specific Gravity of Solutions of CO<sub>2</sub> in Water (distilled).*

| Grammes per 100 c.c. | Sp. Gravity. | Grammes per 100 c.c. | Sp. Gravity. |
|----------------------|--------------|----------------------|--------------|
| 0·02                 | 1·00009      | 0·12                 | 1·00044      |
| 0·04                 | 1·00017      | 0·14                 | 1·00049      |
| 0·06                 | 1·00024      | 0·16                 | 1·00055      |
| 0·08                 | 1·00030      | 0·18                 | 1·00061      |
| 0·10                 | 1·00038      | 0·20                 | 1·00065      |

I submit the above with great diffidence. The work was beset with sources of error, but I believe the figures to be near the truth; and I think that they prove two things:—1st, That carbonic acid raises the density of water; and 2nd, That it does so to just the extent (allowing for experimental error) required to reconcile the two processes in question, for as the average  $\text{CO}_2$  in the above series of beers is 0.1 gramme in 100 c.c., this would raise the gravity of water to 1.00038. The excess of this latter above unity should be added to the “extract” gravity before applying the formula, when the alcoholic strength, as ascertained by the two processes, will be practically identical.

For further proof I treated two more series of beers as before, previously endeavouring to expel all  $\text{CO}_2$ , or as much as possible. The samples were shaken, and exposed to the vacuum of an air pump repeatedly. The following were the results:—

*Specific Gravities at 60° F. (all average figures).*

| No. | Beer.   | Extract. | Alcohol by Tabarie. | Alcohol by distillation. | Difference in favour of Tabarie. |
|-----|---------|----------|---------------------|--------------------------|----------------------------------|
| 5.  | 1.01401 | 1.02206  | 0.99195             | 0.99197                  | 0.00002                          |
| 6.  | 1.01943 | 1.02767  | 0.99176             | 0.99178                  | 0.00002                          |

The  $\text{CO}_2$  in all the above samples averaged less than 0.022 grammes per 100 c.c., equivalent to a density of 1.00009 or under.

These results are in my opinion fairly satisfactory, and go to show that by the complete, or nearly complete, expulsion of the carbonic acid in beer, the direct and indirect processes for the estimation of alcohol therein fairly agree, and that the formula  $1 - (E - B)$  may be safely applied.

In conclusion I have pleasure in acknowledging the assistance of my pupil, Mr. Horace Cox Wheeler, throughout my work.

#### DISCUSSION.

The President remarked that Mr. Harvey had not adopted the Tabarie method, that is to say, the division method, but had used the subtraction formula, which the text-books contended was wrong. He (the President) had calculated, from Mr. Harvey's results, the specific gravity of alcohol by division, and found that the division formula in every case gave results further from the truth than did the subtraction formula, thus confirming Mr. Blunt's contention, which had been endorsed by himself (Mr. Hehner).

He hoped that the outcome of this and the previous discussion on this subject would be the working out of a really correct formula. It was evident that neither of those now in use were based upon real mathematical principles; and what they had to aim at was a really correct expression of what the relation between the specific gravities before and after boiling was to the quantity of alcohol present.

Mr. Harvey replied that he was practically ignored the division formula because he could not find sufficient proof that its results were reliable. His own experiments had



been confined entirely to beer. Whilst admitting that there was little hope of the question being absolutely solved, he might say that at one time he expected that the extract itself might suffer some change and loss of density consequent upon the boiling in order to obtain the alcohol. He had made experiments to prove that by boiling measured quantities under efficient condensers; but, after hours of boiling, he found that the gravity remained unchanged, so that the matter was not susceptible of proof in that way.

Dr. Sykes remarked that there could be no doubt that the "extract" of a beer did undergo a change of gravity by being boiled in an open beaker, since a turbidity or even a deposit formed. In the distillation process, which was conducted out of contact with the atmosphere, the residue in the retort was bright and clear.

### THE ADULTERATION OF BASIC SLAG.

BY BERNARD DYER, *B.Sc. (Lond.)*

IN THE ANALYST for December, 1891, (Vol. xvi., p. 236), there appears an abstract of a paper by Morgen, which deals with the detection of the adulteration of Basic Slag with Redonda Phosphate (phosphate of alumina).

The use of caustic soda solution (originally suggested, I believe, by Richter, *Landwirthschaft: Annalen* XXXV., 1890), is referred to; but the statement is made that "the best method for the quantitative examination of basic slag consists in treating the sample with a 5% solution of citric acid, *in which the phosphoric acid natural to the slag is completely soluble, while that of the Redonda phosphate is not dissolved.*

Both these statements are erroneous, and are likely to lead to confusion if relied upon.

It is true that *raw* Redonda phosphate is only slightly soluble in 5% solution of citric acid, in the case of a rapid treatment, although the solubility is considerable if the treatment is prolonged. *Calcined* Redonda phosphate, however, dissolves to a very considerable extent, and it is calcined Redonda phosphate that is likely to be used. Thus, in an experiment I made, four and a-half per cent. of phosphoric acid was dissolved from calcined Redonda phosphate by cold 5% citric acid solution, standing over night, while by using a warm citric acid solution (about 60°C.), 16% of phosphoric acid (almost half the phosphoric acid present) was dissolved in two hours.

On the other hand, from a finely ground basic cinder, containing 18% of phosphoric acid, only 11% was dissolved during the night by cold treatment, and only 14½% by treatment in the warm for two hours.

Although, therefore, there is no question that the phosphoric acid of basic slag is more readily soluble in 5% citric acid solution than that of Redonda phosphate, there is no such difference between them in this respect as would form the basis of a reliable qualitative test, and any attempt to take advantage of the difference for quantitative purposes is obviously hopeless.

PAPERS READ AT MEETING, NOVEMBER 1TH, 1891.

## NOTE ON TABARIE'S METHOD OF DETERMINING ALCOHOL.

By ALFRED H. ALLEN.

SOME time ago Mr. Thomas Blunt pointed out to me the anomaly of Tabarie's formula for determining alcohol from the extract gravity of the sample, and suggested a formula which he thought would be preferable. In order to throw further light on the matter, I requested Mr. Robert Waterhouse to make a series of experiments. The investigation was interrupted, but the following results were obtained. A sugar solution was made by dissolving 20 grammes of cane sugar in water, and making up the solution to 100 c.c. The specific gravity was carefully taken, and then accurately measured portions of the solution were mixed with (1) an equal measure, (2) a half measure, and (3) a double measure of rectified spirit of exactly ascertained gravity. The volume of the mixture was observed, after which a known measure was distilled off, and the gravity of the distillate taken, while the extract was diluted to its original volume and its specific gravity also observed.

The following results were obtained: -

|  | Expt. 1.  | Expt. 2.  | Expt. 3.  |
|--|-----------|-----------|-----------|
| Measure of sugar solution taken ...                                  | 50 c.c.   | 33 c.c.   | 67 c.c.   |
| Measure of spirit taken ...  | 50 c.c.   | 67 c.c.   | 33 c.c.   |
| Measure of mixed liquid ...  | 97.9 c.c. | 98.1 c.c. | 98.4 c.c. |
| Specific gravity of mixed liquid ...                                 | 0.9764    | 0.9299    | 1.0149    |
| Specific gravity of extract ...                                      | 1.0400    | 1.0227    | 1.0526    |
| Absolute alcohol calculated from }<br>known composition of mixture } | 38.25 %   | 53.59 %   | 24.16 %   |
| Alcohol calculated from specific }<br>gravity of distillate ... }    | 39.16 %   | 54.19 %   | 24.59 %   |
| Alcohol calculated from specific<br>gravity of extract —             |           |           |           |
| By Tabarie's formula: $\frac{L}{E} = S.*$                            | 10.40 %   | 53.91 %   | 25.86 %   |
| By Blunt's formula: $1000 - (E - L) = S.$                            | 41.60 %   | 54.86 %   | 27.22 %   |

I give the results obtained in the third experiment, but there were sources of error which prevent me from laying much stress on the figures.

## NOTES FROM THE KHEDIVIAL LABORATORY, CAIRO.

By H. DROOP RICHMOND.

1. **The Relation between Specific Gravity, Fat, and Solids not Fat in the Milk of the Gamoose.**—In the researches on the milk of the Gamoose, made by Mr. Pappel and myself, we found that the formula I had worked out for cows' milk was not applicable. I have, therefore, worked out one to express the results obtained

\* Where L = specific gravity of liquid; E = specific gravity of extract; and S = specific gravity of spirit, from which its strength can be ascertained by a table.

in the analyses of Gamoose milk; the methods and reasoning employed were exactly the same as those indicated in a former paper (ANALYST xiv., 121). This formula is  $T = .27 \frac{G}{D} + 1.191 F$ . I have also applied the formula for calculating proteids and sugar given in the ANALYST (xv. 170),  $P = 2.8 T + 2.5 A - 3.33 F - .7 \frac{G}{D}$  to the milk of the Gamoose with satisfactory results.

The following table shows the agreement between the fat proteids and sugar found and calculated respectively:—

|     | G    | $\frac{G}{D}$ | T     | F(found) | F(calc.) | Error | Ash | P(found) | P(calc.) | Error | S(found) | S(calc.) | Error |
|-----|------|---------------|-------|----------|----------|-------|-----|----------|----------|-------|----------|----------|-------|
| 1.  | 35.2 | 34.00         | 12.88 | 3.00     | 3.11     | .11   | .88 | 4.21     | 4.46     | .25   | 4.59     | 4.54     | -.05  |
| 2.  | 40.7 | 39.11         | 11.76 | 1.05     | 1.01     | -.04  | .92 | 4.43     | 4.25     | -.18  | 5.18     | 5.54     | .36   |
| 3.  | 23.3 | 22.77         | 10.47 | 3.59     | 3.63     | .04   | .61 | 2.91     | 2.93     | .02   | 3.30     | 3.34     | .04   |
| 4.  | 39.2 | 37.72         | 13.90 | 3.06     | 3.13     | .07   | .90 | 4.44     | 4.57     | .13   | 5.50     | 5.37     | -.13  |
| 5.  | 31.4 | 30.44         | 12.51 | 3.77     | 3.60     | -.17  | .86 | 3.46     | 3.30     | -.16  | 4.27     | 4.58     | .31   |
| 6.  | 37.3 | 35.96         | 16.61 | 5.94     | 5.79     | -.14  | .88 | 3.98     | 3.84     | -.14  | 5.85     | 5.91     | .06   |
| 7.  | 35.8 | 34.38         | 15.47 | 5.24     | 5.20     | -.04  | .86 | 4.11     | 3.93     | -.18  | 5.29     | 5.44     | .15   |
| 8.  | 34.7 | 33.53         | 15.52 | 5.30     | 5.43     | .13   | .83 | 4.01     | 4.38     | .37   | 4.96     | 5.01     | .05   |
| 9.  | 36.7 | 35.40         | 15.80 | 5.15     | 5.24     | .09   | .85 | 4.35     | 4.41     | .06   | 5.22     | 5.39     | .17   |
| 10. | 34.5 | 33.35         | 15.86 | 5.79     | 5.76     | -.03  | .86 | 3.93     | 3.94     | .01   | 5.01     | 5.27     | .26   |
| 11. | 35.7 | 34.47         | 16.35 | 5.91     | 5.91     | —     | .86 | 4.12     | 4.10     | -.02  | 5.18     | 5.48     | .30   |

The whole of these determinations were made very carefully—in duplicate in many cases—by two chemists, the maximum differences being for G .1, for T .08, for F .06, for P .05, for S .02, and for A .04, and for that reason have only these results been used for calculation of the formula, but its correctness has been abundantly proved by other analyses. The probable error between fat found and calculated is  $\pm .08$ , between proteids found and calculated  $\pm .14$  and between sugar found and calculated  $\pm .18$ . The average calculated amount of proteids is .01 too high, while the calculated sugar averages .14 too high. This difference is due to the fact that the milk contains other constituents, and are not sufficiently large, seeing that a very great agreement cannot be expected in this case, to induce me to change the formula.

The figures for the influence on the density of one gram of fat and solids not fat respectively, and for their density in solution, have been calculated as follows from the formula, and are:—

|                | Influence on Density. |     |     |       | Density in Solution. |     |     |       |
|----------------|-----------------------|-----|-----|-------|----------------------|-----|-----|-------|
| Fat            | ...                   | ... | ... | -.708 | ...                  | ... | ... | .934  |
| Solids not fat | ...                   | ... | ... | 3.705 | ...                  | ... | ... | 1.589 |

The average percentage composition of the solids, not fat, is:—

|                  |     |     |     |     |      |
|------------------|-----|-----|-----|-----|------|
| Proteids         | ... | ... | ... | ... | 40.8 |
| Ash              | ... | ... | ... | ... | 8.2  |
| Sugar            | ... | ... | ... | ... | 49.5 |
| Other Substances | ... | ... | ... | ... | 1.5  |

Showing a proportion of 6:5:1 for Sugar, Proteids, and Ash respectively.

**2. The Estimation of Iodoform.**—When Iodoform is heated with alcoholic soda it is split up with the formation of Sodium Iodide, Sodium Formate and other substances; the proportions appear to be that  $16\text{CHI}_3$  require  $42\text{NaOH}$ , and give  $35\text{NaI}$  and  $4\text{KHCO}_2$ ; the estimations made were as follows: for 100 parts Iodoform:—

|                  | Found.       | Calculated from above proportions. |
|------------------|--------------|------------------------------------|
| Soda             | 26.4         | 26.6                               |
| Iodine as Iodide | 69.3 to 70.4 | 70.2                               |
| Formic Acid      | 3.34         | 2.92                               |

These figures show that the re-action is a complex one, and I have not attempted to construct an equation to express the changes which take place; with the assumption that for every 100 parts of Iodoform 70 parts of Iodine are produced as Iodide, a fairly reliable method of working is possible; about .1 — .15 gram of Iodoform, or such quantity of the substance to be examined as will give that quantity, is weighed out and dissolved in alcohol, an excess of alcoholic soda is added, and after about ten minutes' digestion near the boiling point of the alcohol, the excess of alcohol is evaporated; the residue is taken up with water, made slightly acid with *dilute* nitric acid and a small quantity of calcium carbonate added to restore neutrality. The solution is then titrated with the solution of nitrate of silver used for water analysis (of which 1 c.c. = .005418 gram Iodoform), an excess of about .3 c.c. is required to produce a good end reaction with chromate of potash and this should be subtracted.

The following test analyses show the reliability of the method:—

|                                 |                           |                         |
|---------------------------------|---------------------------|-------------------------|
| .126 grs. Iodoform took         | 23.4 c.c. Silver Solution | = .1268 grs. or 100.1 % |
| .141 " " "                      | 25.75 " "                 | .1395 " or 99.0 "       |
| .0995 " " "                     | 18.5 " "                  | .1002 " or 100.7 "      |
| 2.203 " of an 8.5% mixture took | 34.6 " "                  | .184 " or 8.4 "         |
| 1.8385 " " " "                  | 29.6 " "                  | .1575 " or 8.5 "        |

The method does not take more than about half an hour to perform, and is therefore practical. Should the iodoform be obtained in ethereal solution, as for instance, in the estimation of acetone, the ether need not be evaporated, but can be mixed directly with the alcoholic soda. No danger of loss of iodoform need be feared, and it is not necessary to use an inverted condenser.

**3. The Testing of Petroleum.**—For testing petroleum in hot climates I have found that the differences owing to the higher temperatures in the flash point may be almost entirely done away with by cooling the bottle containing the sample, before it is opened, down to a low temperature, say  $10^\circ$ , for about an hour before the test is taken. Thus, samples of petroleum gave the following flash points:—

|                    |                    |       |       |       |       |
|--------------------|--------------------|-------|-------|-------|-------|
| Temperature of air | $15^\circ\text{C}$ | 18.5° | 22.5° | 24.5° | 25.0° |
| " "                | $29^\circ\text{C}$ | 18.5  | 22.5° | 24.0° | 24.5  |

By burning petroleum in an ordinary lamp, and observing the loss of weight, and

testing the petroleum at each 5 per cent., I find, on the average, that the flash point is raised  $2^{\circ}$  for each 5 per cent. lost up to about 25 per cent., when the rise in the flash point becomes slightly less. As the lamp burns lower down the space becomes more and more filled with air, but there is less tendency to ignite. When half has burnt away, there is a flash point of from  $15^{\circ}$  to  $18^{\circ}$  higher than at the commencement.

When petroleum is distilled, at a certain temperature it "cracks" or decomposes. By cautious fractional distillation, this point may be determined with very fair exactitude. I use a flask of about 150 c.c. capacity, with a neck six inches long up to the side tube, and distil at the commencement with a small flame, just sufficient, so that the distillation will nearly stop at  $150^{\circ}$ . I then increase the flame, so that the distillation nearly stops at  $270^{\circ}$ . I then again increase it slightly till the temperature, after rising steadily, suddenly goes down  $20^{\circ}$  or so, and remains there. This point I call the cracking point: it is usually about  $300^{\circ}$ , but with good petroleum may be higher.

I quote two experiments in duplicate, to show how exact the results are:—

|   | 3%              | $2\frac{1}{2}\%$          | 1%              | $\frac{1}{2}\%$ |
|---|-----------------|---------------------------|-----------------|-----------------|
| Below $120^{\circ}$                         |                 |                           |                 |                 |
| From $120^{\circ}$ — $150^{\circ}$          | 16              | 15                        | $13\frac{1}{2}$ | 13              |
| 150 — $270^{\circ}$                         | $52\frac{1}{2}$ | $51\frac{1}{2}$           | 57              | 57              |
| $270^{\circ}$ to cracking pt. $295^{\circ}$ | $70\frac{1}{2}$ | 70 (c. p. $297^{\circ}$ ) | $72\frac{1}{2}$ | 69              |

### The Determination of Silica in Substances containing Fluorine.

**W. Hampe.** (*Chem. Zeit.* 1891, xv. 1521, 1522.)—The determination of silica, in minerals containing fluorine, can be effected in the manner prescribed by Berzelius, or by the method used by Rose, or by the one elaborated by Fresenius and Hintz. Berzelius opens up the substance by fusion with soda, dissolves out the melt with water, and determines the silica both in solution and in the residue. Fresenius and Hintz in their process, which is specially designed for testing cryolite, decompose the substance by heating with strong sulphuric acid in a lead tube in a stream of dry air, and receive the hydrofluoric acid and the silicon fluoride which are evolved in ammonia. The contents of the lead tube are then extracted with water, and the residue attacked by fusion with soda. The further treatment of the fusion is in accordance with that obtaining in Berzelius' method.

In the case of a substance containing both silica and fluorine, which cannot be opened up either by fusion with sodium carbonate or caustic soda, nor by heating with strong sulphuric acid, neither the process of Berzelius nor that of Fresenius is available. The principle of the latter may be retained by using a platinum apparatus of such construction, that the substance may be fused in it with potassium bisulphate, and the evolved silicon fluoride quantitatively absorbed. The construction of such an apparatus, however, presents difficulties.

Since the determination of silica in strongly-ignited alumina containing fluorine,

which cannot be attacked either by sodium carbonate or by sulphuric acid, is of much technical importance in the manufacture of aluminum, the following process has been devised by the author.

0.5 to 1 gm. of the substance is fused with 8 to 10 times its weight of anhydrous borax, free from silica. The finely-powdered borax is placed in a thin layer at the bottom of a platinum crucible and pressed down; an intimate mixture of the weighed portion of substance with borax is then added, the whole covered with a fresh layer of borax, and fused for about twenty minutes. A perfectly clear melt results. The melt is poured into a platinum basin, covered while cooling with the crucible in which the fusion has been conducted, and treated with hot water until both the main portion and the residue in the crucible are thoroughly disintegrated, a process which takes as a rule a couple of days. Half as much ammonium chloride as the weight of the borax originally taken, is then added to the contents of the platinum basin, the mixture warmed until it no longer smells strongly of ammonia, and the silica, together with aluminium and possibly calcium borate, filtered through a platinum or caoutchouc funnel and well washed. The filtrate is evaporated to dryness in a platinum basin, heated to a temperature somewhat above  $100^{\circ}\text{C}$ ., and dissolved again in water. The solution is acid in reaction from the presence of boric acid, and possibly also of hydrochloric acid, which have been liberated by the dissociation of ammonium borate, or ammonium chloride, during the evaporation. It is made slightly alkaline with ammonium carbonate and the precipitate filtered off. The filtrate is again evaporated and the operation repeated until no further precipitate is obtained. The combined precipitates are dried, the filter paper ignited, and the whole fused with four times its weight of sodium carbonate; the melt treated with excess of hydrochloric acid, evaporated to dryness, taken up with dilute hydrochloric acid, and the silica filtered off. As in all silicate analyses, in order to obtain an exact determination of silica, it is necessary to evaporate the filtrate again to dryness, treat once more with hydrochloric acid and water, and ascertain whether any further trace of silica has been thus separated. (Note by Abstractor. It is well known that where the filtrate from the silica is not needed, its separation can be effected by evaporation with sulphuric acid rather than with hydrochloric acid, the quantity left in solution being inconsiderable when the former is used; the need for repeated evaporation is thus obviated.)

The purity of the silica is ascertained, after weighing, by treatment with hydrofluoric acid in the usual manner.

The following experiments were carried out in order to make sure that an exact determination of silica was practicable even in the presence of a large quantity of fluorine: selected pieces of pure cryolite were powdered and examined for silica, then mixed with a weighed quantity of silica prepared from a silicate, and the mixture analysed by the foregoing process. No ponderable quantity of silica was found in the cryolite used; in the test analysis the quantity of silica recovered was within a few

milligrams of that added. Thus 0.6142 grms. of cryolite were taken, and 0.5135 grms of silica added; the silica found amounted to 0.5100 grms.

A sample of ignited alumina containing fluorine gave the following results :

|            | (1)   | (2)   | (3)   | Average. |
|------------|-------|-------|-------|----------|
| Silica ... | 3.95% | 3.79% | 3.98% | 3.907%   |

A determination of the contents of aluminium was also made as a check. For this purpose the substance was fused with potassium bisulphate, whereby a portion of the silica, corresponding to the amount of fluorine present, was volatilised as silicon fluoride. The melt dissolved clear in dilute sulphuric acid. The solution was evaporated until fumes of sulphuric acid were given off, by which means a part of the silica was rendered insoluble. After cooling, water was added, and the solution filtered. The filtrate may be termed A and the residue B. The residue B was then treated as in the analysis of the silicate, that is fused with soda, etc. The filtrate from the pure silica thus obtained gave with ammonia a small precipitate of alumina. The filtrate A was precipitated with ammonia the usual precautions being observed, the precipitated alumina and silica filtered off, dried, ignited, and fused with sodium carbonate. The melt was dissolved in hydrochloric acid, the solution evaporated to dryness, the residue treated with strong hydrochloric acid, the silica remaining undissolved filtered off, and the alumina precipitated with ammonia in the filtrate. Both portions of silica from A and B were examined as to purity after weighing. The results were :

|                            |     |        |
|----------------------------|-----|--------|
| Total alumina from A and B | ... | 95.50% |
| „ silica „ „               | ... | 3.08%  |

The quantity of silica volatilised as silicon fluoride by fusion with potassium bisulphate was therefore  $3.907 - 3.08 = 0.827\%$ . From these data the amount of fluorine in the substance may be calculated as  $1.051\%$  and the complete composition as follows :

|                    |          |
|--------------------|----------|
| Alumina            | 94.563%  |
| Aluminium fluoride | 1.548%   |
| Silica             | 3.907%   |
|                    | 100.018% |

B. B.

**The Action of Water on Glass Vessels for Chemical Use.** F. Mylius and F. Foerster. (*Zeits. Instrumentenk.* 1891, xi. 311. *Through Chem. Zeit.*)—The authors have already shown that the greater part of the matter dissolved out of glass by water consists of alkalis, and the quantity of alkali dissolved is a measure of the quality of the glass. When the quantity is greater than 0.1 of a mg., it can be directly determined by titration with  $\frac{n}{1000}$  sulphuric acid. Smaller quantities are best estimated by

shaking with an ethereal solution of eosin, which becomes red, the intensity of the colour being proportional to the amount of alkali present. The comparison of one glass with another can be effected by treating the vessels to be tested with water at 20° C. for three days, in order to bring their surfaces into a normal condition, emptying them and allowing them to be acted upon for a second period of three days by pure water prepared by re-distilling ordinary distilled water with a little sulphuric acid to retain the traces of ammonia that are otherwise invariably present. The alkalinity of the water that has been in contact with the glasses to be tested is then determined in the manner described above.

As the result of their observations the authors come to the following conclusions:—

1. The action of cold water upon glass is at first very rapid, but its rate rapidly decreases; the retardation is due to the production of a layer of glass that has been already extracted, and is but slightly permeable.
2. The strength of the attack of water on glass is influenced by its condition as regards disintegration or exfoliation.
3. The relative attackability of the same glass varies according as hot or cold water is used.
4. The process of boiling out a glass vessel is of great utility, though its usefulness is diminished if the glass be bad.
5. Glass surfaces have the property of absorbing alkali from solution and retaining it in spite of ordinary rinsing; long contact with water is necessary to remove it. B. B.

**The Coloration of Preserved Foods with Copper.** Tschirch. (*Read at the 64th meeting of the Deutsch. Naturforsch. u. Aerzte. Through Chem. Zeit.*)—The time-honoured method of imparting a beautiful green colour to preserved foods consists in treating the articles to be colored with a solution of copper sulphate, which is quickly poured off and the last traces removed by repeatedly washing with water; the preserved articles are then boiled and the vessels containing them soldered up. The colouration results from the formation of the copper salt of an acid derived from phyllocyanin. This body is very inert, is insoluble in water, hydrochloric acid and acetic acid, soluble in alcohol, and indifferent to the action of light. As the quantity is quite small, only a few milligrams in 100 grams, the author is disposed to tolerate the practice. B. B.

**The Valuation of Oil of Cloves.** H. Thoms. (*Read at the 64th meeting of the Deutsch. Naturforsch. u. Aerzte. Through Chem. Zeit.*)—The value of oil of cloves for medicinal purposes depends wholly on its content of eugenol, while for the purposes of the perfumer regard must also be had to the amount of sesquiterpene present. The method used by the author for the determination of the former is based upon the production of benzoyl eugenol,  $C_{10}H_{11}O_2 \cdot C_7H_5O$ . In a preliminary experiment with pure eugenol 99.25 per cent. of the theoretical quantity of the benzoyl derivative was obtained. When sesquiterpene is present, as in oil of cloves, the process is carried out as follows: 5 grms. of the



sample are treated with 20 grms. of caustic soda solution [15 per cent.] and 6 grms. of benzoyl chloride added; the mixture vigorously shaken, during which operation a considerable amount of heat is evolved, allowed to cool, 50 c.c. of water added, heated until the crystalline ester has become liquid, and again allowed to cool. The aqueous liquid is then filtered off and the residue repeatedly washed with water, heating and cooling at each washing. The removal of the sesquiterpene is effected by treating the crystalline mass with 25 c.c. of 90 per cent. alcohol, heating on the water bath, shaking well to break up the cake, cooling to 17° C., filtering and collecting the filtrate in a graduated cylinder. The total bulk of the filtrate and washings should be 25 c.c. The precipitate of benzoyl eugenol is dried at 100° C. to constant weight. A correction 0.55 grms. for the benzoyl eugenol dissolved by the alcohol must be made. Calling (a) the amount of the benzoyl found and (b) the quantity of oil of cloves taken, the percentage of eugenol in the sample is represented by the expression:—
$$\frac{4100 [a + 0.55]}{67b}$$

The examination of a large number of samples of oil of cloves showed that the content of eugenol varied from 76.8-90.64 per cent. It further appeared that the specific gravity rose and fell with the percentage of eugenol. The author also found that oil obtained from the stalks of the plants yielding oil of cloves, containing 83.2 and 84.88 per cent. of eugenol, had the low specific gravities of 1.059 and 1.062. He is, therefore, of opinion that oil from this source which has hitherto been accounted of little worth, has been undervalued, and that its low specific gravity is due to the presence of some substance other than the eugenol and sesquiterpene present in normal oil.

B. B.

**A New Process for the Determination of Phenol.** L. Carre. (*Compt. Rend.*, 1891, cxiii., 139, through *Chem. Zeit.*).—The process depends on the conversion of phenol into picric acid, and the colorimetric estimation of this body by means of its sodium salt. 10 grammes of pure phenol are weighed, made up to 1 litre, and from this solution others containing 5, 4, 3, 2, 1, 0.8, 0.6, 0.4, 0.2, 0.1 grammes of phenol per litre prepared. 25 c.c. of the solution containing the phenol to be estimated, taken after dilution if necessary, are heated with 5 c.c. of nitric acid in a small flask on the water bath for 1—2 hours, the standard being treated in precisely the same way; a preliminary trial shows which of the standard solutions approximates to the sample being tested. In order to obtain greater accuracy 20 c.c. of soda solution are added to the contents of the flask after heating, the liquid made up to 50 c.c., filtered, and compared in the colorimeter with the standard to which it is nearest in tint. The use of concentrated solutions should be avoided. Should the liquid in which the phenol is to be estimated contain a little alcohol it is best to heat for some time after the addition of nitric acid; in the event of a considerable quantity of alcohol being present, it must be diluted to avoid the formation of ethyl nitrite. When impure phenol is to be estimated, the heating must be prolonged to decompose the accompanying tarry matter.

B. B.

**The Eschka Method of Determining Sulphur in Coal.** J. Rothe. (*Mitt. Königl. tech. Versuchs.*, 1891, ix., 107, through *Chem. Zeit.*).—Eschka's method consists in heating 1 grm. of coal with 15 grms. of a mixture of two parts by weight of magnesia and one of dry sodium carbonate in a 30 c.c. platinum crucible, placed in a sloping condition, so that only the lower part is red hot. The mixture is stirred two or three times in the course of an hour, at the end of which time the coal is fully burned off. Solution in hydrochloric acid, oxidation with bromine, and precipitation with barium chloride completes the operation. The author finds that no loss of sulphur occurs, and that, where several determinations have to be made, porcelain crucibles heated in a muffle for 20—30 minutes can be advantageously substituted for the platinum crucible and the bunsen burner.

B. B.

**The Recognition of Arsenic.** J. Thiele. (*Liebigs Annalen*, 1891, cclvi., 55, through *Chem. Zeit.*).—Arsenic in whichever state of oxidation it may be, can be recognised in the presence of antimony and tin by strongly acidulating the solution containing it with hydrochloric acid, and adding at least 1 gram. of sodium hypophosphite to 10 c.c. of solution. On warming in the water-bath, the arsenic is precipitated as a brown or brown-black powder. Very dilute solutions need heating for thirty minutes, and a coloration instead of a precipitate may be produced. The reaction does not take place in solutions acid with sulphuric acid in the absence of a halogen acid. Its sensitiveness is increased by the addition of a crystal of potassium iodide, 0.025 mgm. of arsenic being detectable, whereas the limit in the absence of the iodine is 0.05. The "noble metals" and copper must be absent; bismuth and antimony are only precipitated in strong solutions; the addition of potassium iodide should be omitted if the former be present, on account of the strong yellow colour of bismuth iodide. In the presence of much iron the solution should be covered to prevent free access of air, as otherwise it will become yellow. A separation of antimony and arsenic cannot be based on this reaction, as the precipitate is too easily oxidisable.

In using Marsh's test, the addition of platinum chloride to aid the solution of the zinc should be avoided, as arsenic is retained thereby apparently as an arsenide of platinum (?)

According to Brauner and Tomiczek, arsenic is precipitated as pentasulphide from a warm acid solution of arsenic acid, when a rapid stream of sulphuretted hydrogen is used. With a slow stream a mixture of  $As_2S_3$  and  $As_2S_5$  comes down. A cold solution in strong hydrochloric acid gives a mixture of  $As_2S_3$ ,  $As_2S_5$  and S, and a rapid stream of the gas, if diluted, gives the same result as a slow stream.

B. B.

**Desiccators.** W. Hempel. (*Pharm. Centr.*, 1891, xii., 453, through *Chem. Zeit.*).—The author lately advanced the view that the drying material in a desiccator was more effective when placed above instead of below the substance to be dried, a conclusion which was contested by Biltz. He now finds that in the case of desiccators, large in

proportion to the vessel containing the substance to be dried, and supplied with a considerable quantity of concentrated sulphuric acid in proportion to the amount of water to be absorbed, the time occupied in drying is but little shortened, but that under contrary conditions the process is much hastened. Thus 10 c.c. of water in a dish, large in proportion to the desiccator, were absorbed by 25 c.c. of sulphuric acid in three and a half days when the acid was placed above the water, while when placed below the time was six and a quarter hours.

B. B.

**Examination of Peppermint Oil.** H. Andres. (*Pharm. Zeits. Russ.*, 1891, xxx., 417, through *Chem. Zeit.*).—Commercial samples of peppermint oil differ in quality as well as in composition. The determination of the iodine number is a useful means of discrimination, being smaller, the richer the oil is in menthol, the chief active constituent of the oil. The following are some figures thus obtained:—English, 52.9, German, 69.7, American, 72.3, and Russian, 96.8.

B. B.

**Examination of Tanning Extracts.** F. Jean. (*Moniteur Sci. Quesneville*, 1891, 59J, 918.)—In a paper which describes a new apparatus for extracting tannins from tanning-stuffs, of technical interest only, the author lays down that the analysis of a tanning extract should include the determination of (1) the specific gravity, both absolute and in degrees Beaumé, (2) the matter insoluble in cold water, which should not exceed 2 per cent. except in quebracho extract which may be allowed to contain 3—4 per cent., (3) acidity due to organic acids and that due to mineral acids, (4) contents of tannin and of gallic acid, (5) matter absorbable by hide, (6) extractive matter, (7) heavy adulterants added to increase the specific gravity.

As the value of a tanning material largely depends upon the colour which it will impart to the leather, those materials being most valuable which occasion the least departure from the buff of oak-tanned leather, the author aims at obtaining some evidence on this point. He immerses cuttings of parchment or unhaired skin, previously plumped in water, in a solution of the extract at  $\frac{1}{2}^{\circ}$  Beaumé for 30 hours, the liquor being changed at the end of the first 12 hours; the samples are then exposed to the air and compared with standard samples, similarly treated in known extracts.

A. G. B.

**A Delicate Test for Alum in Potable Water.** Ellen H. Richards. (*Technology Quarterly*, iv., 194–195.)—To 25 c.c. of the water (concentrated from one litre or more, if necessary), are added a few drops of freshly-prepared logwood decoction; any alkali is neutralised and the colour brightened by the addition of two or three drops of acetic acid. By comparison with standard solutions the amount of alum present may be determined. It is said that 1 part per million of alum can be detected with certainty in this way. The logwood chips must be treated with boiling water two or three times before finally extracting for the colour, as the first extraction gives a yellow colour, the third or fourth a deep red.

A. G. B.

**The Use of Potassium Ferrocyanide and Ferricyanide in Analysis.**

**C. Luckow.** (*Chem. Zeit.* 1891, xv. 1491, 1492.)—The author being alive to the objections to the use of potassium ferrocyanide in such analytical operations as the determination of zinc, has turned his attention to the question of the availability of potassium ferricyanide for like uses, and records the following facts.

Zinc can be determined in a solution acidulated with nitric or acetic acid, with exactitude, even in the presence of lead, by means of potassium ferricyanide, either gravimetrically or volumetrically, while the lead can be estimated in the filtrate in a similar manner by potassium ferrocyanide. Stannic oxide can be determined by potassium ferrocyanide in the presence of antimonious acid and arsenious acid in a solution which has been evaporated with oxalic acid, a little dilute sulphuric acid having been added subsequently.

In carrying out such operations it must be remembered that potassium ferrocyanide is liable to contain, besides sulphates and chlorides, sodium salts, as pointed out by L. Blum. This is of no importance if the solution be standardised upon a metallic solution of known value, always provided that the solution to be titrated contains no metal capable of yielding a precipitate with either of the first-named impurities. In the contrary case, as well as in those instances where it is required to determine the composition of the precipitate from the amount of potassium ferrocyanide solution used, a perfectly pure salt is necessary: the like is true of potassium ferricyanide. Potassium ferrocyanide is stable in the dry state, and its solutions are unaltered by cautious evaporation. Daylight, and especially direct sunlight, appear, however, to act slightly upon its solutions as noted by Moldenhauer, who adds a small quantity of caustic potash to preserve them. Potassium ferricyanide is more sensitive to the influence of temperature and light than ferrocyanide, on which account it is kept in brown glass bottles, both when it is in the solid state and in solution, and should be subjected to no higher temperature than 50°–60° C. when recrystallised. The cautious addition of chlorine suffices to convert any ferrocyanide that may be present into ferricyanide. The purity of a solution of potassium ferricyanide may be proved by the addition of a solution of an uranium salt, which gives a red-brown coloration should ferrocyanide be present, or of a lead salt which gives a white precipitate in the same contingency.

The volumetric determination of various new metals by means of potassium ferrocyanide and ferricyanide must be effected with the aid of some external indicator.

Of these, there are two classes, the first being those which indicate whether the metal, being titrated, is completely precipitated or not, while the second are such as react with an excess of the precipitant. Among the first are the alkaline sulphides, and the ferrocyanide and ferricyanide; for metals which give brown-black or black precipitates with alkaline sulphides, a mixture of a pure zinc salt with ammonia, ammonium sulphide, and a little rosolic acid or similar colouring matter may be used; the function of the rosolic acid is to make the edge of the streak made on the paper used in carrying out the test more easily discernible. To the latter belong substances which give a brightly

coloured precipitate with ferro- and ferricyanides; such are ferric and cupric salts for the former, and ferrous and cobalt salts for the latter. The author has found cupric acetate acidified with acetic acid, or ammonium ferrous sulphate to which a little ferric chloride has been added, useful for these purposes. The solution to be titrated should in general measure 20 to 30 c.c. and contain 0.1 to 0.15 grm. of the metal to be determined. When it is desired to filter off the liquid from which a metal such as zinc has been precipitated by a solution of known strength, and to determine the excess of the precipitant in the filtrate, it will be found advisable to use potassium ferricyanide rather than ferrocyanide in many cases; the precipitates produced by it filter more easily. B. B.

**The Coloring of Preserved Foods. A. Tschirch.** (*Schweiz. Wochenschr. Pharm.* 1891, xxix. 344, through *Chem. Zeit.*).—The green coloring matter of leaves, etc., is extremely sensitive both to light and to acids of every kind. In order to hinder its decolorisation, sodium carbonate is commonly added to green vegetables before cooking, by which treatment free acids are neutralised, and also such salts as potassium acid-oxalate. Not only is the action of the acids upon the chlorophyll thus prevented, but a relatively stable sodium salt, green in colour, is formed, enhancing the effect. The question of the coloring of preserved foods by means of copper sulphate has also been investigated by the author, and the conclusions he arrived at recorded in *THE ANALYST*, xvi., 200. B. B.

**The Use of Calcium Sulphate in Dialysis. G. Morales.** (*Amer. Journ. Pharm.* 1891, lxiii. 425, through *Chem. Zeit.*).—Herrera suggested years ago the use of dried calcium sulphate in dialysis, the solution to be dialysed being hung in parchment paper in a mass of the powdered substance; the colloids remain in the parchment paper vessel and the water and the crystalline substances pass into the plaster. The method can well be used for the extraction of organic acids from their solution, and in a similar manner, for alkaloids. The author has tried the process for obtaining the alkaloids from opium with but little success, and considers it unsuited for quantitative determinations, although available for qualitative examinations. B. B.

**Poisonous Metals in Preserved Foods. W. Reuss.** (*Chem. Zeit.* 1891, xv. 1522, 1523 and 1583.)—The fact that the amount of lead in the tin coating of vessels for preserved foods, and that in the solder with which they are united, have been limited by law in Germany to 1 per cent. and 10 per cent. respectively, has caused the adoption of vessels closed without a soldered joint, a rubber ring being substituted instead. The

author having observed that preserved foods contained in vessels of this description which appeared unexceptionable, were often contaminated with lead, has examined into the cause of its presence, and finds it to be due to the rubber ring employed.

The following examples are chosen from among the figures quoted by him: (1) Indiarubber rings made in Paris and used by a large German firm, (a.) average weight of ring, 0.5 gm.; ash 66.6 per cent. consisting almost wholly of red lead; no antimony sulphide was present. (b.) An experiment was made by exposing a rubber ring to water under pressure at a temperature of a  $110^{\circ}$  to  $112^{\circ}$  C. for thirty minutes; at the end of this time the ring was found to be much softened and 0.0286 grms. red lead (misprinted  $Mn_2O_3$  in original) was suspended in the water, which contained no lead in solution. (c.) Another ring was similarly treated in the presence of 0.5 kilo. of asparagus. The solution gave an immediate precipitate of lead sulphate on the addition of sulphuric acid; the quantity of lead in solution corresponded to 60 per cent. of the total amount in the ring. (2) Indiarubber rings taken from tins of Australian meat from a large English firm had the same composition as those mentioned under (1). (3) Red rubber rings from Vienna contained 63 per cent. of ash, the bulk of which was red lead. (4) Red rubber rings from a German factory gave similar results, save that a little antimony sulphide was present. (5) Numerous analyses of rings from other German firms gave similar figures.

In view of these facts the author is interesting himself in the manufacture and use of rings of a less poisonous character.

B. B.

**Porcelain Water Baths.** W. Dittmar. (*Chem. Zeit.* xv. 1891, 1467.)—Ordinary copper water baths easily become corroded, and are difficult to keep in a presentable state. The conventional hemispherical variety of porcelain water baths, which used to figure in chemical lists, has never been popular, presumably on account of their supposed fragility, and now appear to be driven out of the market. Kaehler and Martini, of Berlin, have supplied the author with a porcelain water bath of practical utility, consisting essentially of a cylindrical porcelain jar, with a set of concentric rings, also of porcelain, and provided with a tubulus near the bottom, by which connection is made with a constant feeding arrangement, consisting of an inverted flask of water dipping into a small cylindrical vessel coupled direct to the tubulus. The bath is heated by a common ring burner, and is in no way liable to fracture, if reasonable care be taken of it. Evaporations can be conducted in a dust-free atmosphere by the addition of a simple fitting, consisting merely of a glass shade, such as is used for statuettes and the like, resting on a V-shaped gutter having an exit tube attached to it, which carries off the water allowed to flow on the top of the glass shade. This is distributed evenly by means of a couple of strips of paper placed crosswise.

B B.

## LEGAL.

## IMPORTANT DECISION ON A CASE OF MILK ADULTERATION.

(From the *Times*.)

Queen's Bench Division. (Before LORD COLERIDGE and MR. JUSTICE WRIGHT.)

Dyke, Inspector for the Vestry of St. George's, Hanover Square, Appellant.

Gower, Respondent.

THIS case raised an important question under the enactment in the Adulteration Act of 1875 with respect especially to the adulteration of milk. It was an appeal against a refusal by Mr. de Rutzen to convict under the Act a milk seller who had sold milk from which 33 per cent.—one third—of the fatty matter or cream was abstracted, the excuse being that it is of the nature of cream to settle at the top or on the surface of the milk, and that as it is taken out by the measures put in to serve the earlier customers, the milk is necessarily impoverished for the later customers. The question was whether this was an excuse under Section 9 of the Act, which runs in these terms:—"Any person who shall, with intent that the same shall be sold in its altered state, abstract from it any part so as to affect injuriously its quality, substance, or nature, and any person who shall, without notice, sell any article so altered, without making a disclosure, shall," &c. In the present case the question arose whether the selling must be with the intent previously mentioned. It had arisen under these circumstances. The defendant was a milkman, and an officer appointed by the vestry went to his shop and purchased some milk, which being analysed, it was found that 33 per cent. of the fatty matter had been abstracted. Upon the summons this was not denied, but it was urged that it was accounted for by the way in which the milk was sold. It was received in a large vessel, a churn, containing 16 gallons, and it was dealt out to customers in quart or pint measures, and as the cream tended to settle at the top of the milk as the milk was thus taken out, unless it was kept constantly mixed the later customers would find the quality of the milk deficient. The magistrate so found and considered the case sufficient, and so refused to convict, and dismissed the complaint. The vestry appealed, and he stated a case.

Mr. M'Call, Q.C. (with Mr. Arthur Gill and Mr. Stephenson), appeared on their behalf and argued in support of their appeal. The magistrate, he said, was wrong in his view and ought to have convicted. He mistook the scope of the enactment, the object of which was to throw upon the defendant the onus of showing a defence. The second part of the enactment is distinct from the first. [Lord Coleridge.—But the intent in the first part is to be imported into the second?] It is conceived that it is not. If that view be adopted and this defence is supported, as it can always be set up, the object of the enactment will be defeated. [Mr. Justice Wright.—You have not alleged the milkman's knowledge of the deterioration.] Upon the view submitted to the Court it was not necessary to allege it, and the information was so framed as to raise the question. It is one of great interest and importance under the Act, for the practical efficiency of the enactment entirely depends upon it. There is no defence allowed under the Act except a purchase by seller under a warranty, unless there has been a disclosure. He cited "Webb

v. Knight," 2 Q.B.D. 530 ; "Payne v. Boughtwood," 24 Q.B.D. 353 ; "Betts v. Armistead," 20 Q.B.D.

Mr. D. Hart, on the part of the milk seller, the defendant, said he quite agreed that the question raised in this case was one of great public interest and importance with reference to the sale of adulterated articles of food, and especially as to milk. It is not alleged that the milk seller knew of the deterioration of the milk sold, and unless he knew of it, how can he make a disclosure of it? There must be the intent to sell an article deteriorated in quality. [Lord Coleridge.—The intent is quite indifferent to the purchaser, and how can he dive into the man's mind and show his intent? If the alteration in the article is once made, then the sale of it is surely the offence? The seller knows of the alteration, and he sells the article, knowing the alteration. Is that not selling with intent to sell the article as altered?] It is submitted that that is not the meaning of the section ("Nicholls v. Hall," 8 Law Reports, C.P. 322.) [Lord Coleridge.—But how can you get over the decision in "Payne v. Boughtwood," 24 Q.B.D. 353—that a person selling the altered article could be convicted, though at the time he did not know of the alteration?] It is submitted that it is distinguishable, and that it is of no authority, as it was only argued on one side. No attempt was made in that case to show how the alteration came about. [Lord Coleridge.—That distinction is rather against you, for in this case it is known how it happened and the milk seller must have known of it.] That does not appear. [Lord Coleridge.—Can you contend that a milk seller does not know that cream settles on the surface?] Unless it is kept stirred up. [Lord Coleridge.—And it was not sold so stirred up.] That is not stated. [Lord Coleridge.—But the very defence set up shows that it is so, and that the defendant knows it is so.] If that view be taken the milkman may always be convicted. [Lord Coleridge.—If it does not prevail he never can be convicted. He may take off all the cream and sell the impoverished milk, and then say, "Oh, it has been taken by earlier customers." This Act is intended if possible to secure to the people pure milk, and if your view be adopted the object of the Act will be defeated.]

The Court came to the conclusion that the magistrate was wrong, and ought to have convicted.

Lord Coleridge, in giving judgment, said:—We think the magistrate was wrong. The case shortly stated was this. The milk seller has bought milk which we will assume has come to him pure and good. He puts it into a large vessel from which he sells it out in smaller quantities. It is stated in the case that unless the milk is kept stirred there is a tendency of the cream to rise to the top, and so leave the milk below deprived of the richer element. The milk seller knows this, and he sells the milk in that condition. Possibly he may not gain by this if he sells the upper and richer portion of the milk at the same price as the lower and poorer portion. But the Act is passed for the benefit not of the seller but of the buyer, and to secure, as far as legislation can secure it, that he shall have genuine milk with its due proportion of the richer element. Now here it is admitted that—I do not say fraudulently, but by the operation of a known law of



nature—the milk sold to the complainant was 33 per cent. lower in the richer element than it ought to have been. It is obvious that, if the contention of the defendant, the respondent, could prevail, this would inevitably follow (nothing being done to prevent it)—that the upper part of the milk sold would be of a better quality, and that the lower part would be deficient in the richer element to the extent of one-third. And that is, in fact, what happened here, and the question is whether it is an offence under the enactment in the Act (38 and 39 Vict., c. 63, s. 9), which enacts that “No person shall abstract from any article of food any part of it so as to affect injuriously its quality,” &c. Now here, undoubtedly, the defendant had, in fact, abstracted from the milk a part of it so as to affect its quality injuriously. Intentionally or not he had done it; and then it is further enacted, “No person shall sell an article so altered by the abstraction of some part of it so as to affect its quality injuriously without a disclosure.” And here the defendant certainly had sold the altered article without disclosure. It is said that no offence was committed, because the first part of the clause says that no person shall do it with intent to sell without notice, and that therefore the contention is that, however much a person may have altered the article, yet if at the time he altered it he did not contemplate selling it, he had a right to sell it whatever its state. But that would make utter nonsense of the Act, and would deprive the public of its protection. What does it signify to the purchaser of any article which he finds to be adulterated, with what intent the milkseller altered it? And how can it be material for him to dive into the mind of the seller and show what was passing in it when he made the alteration? It is obvious that the injury to the purchaser and the public is the same, and that such a construction would make utter nonsense of the Act. I should therefore have so held quite independently of the case of “*Pain v. Boughtwood*,” which is directly in point, and appears to have been well decided. I think, therefore, that the magistrate was wrong, and that the appeal must be allowed.

Mr. Justice Wright concurred. If, he said, there could be any doubt if section 9 stood alone, there could be no doubt when it was looked at in connection with previous decisions. It had been held in several cases that knowledge was not material (“*Fitzpatrick v. Kelly*,” 8 Law Reports, Q.B., and “*Roberts v. Evans*,” Law Reports, 9 Q.B.). The Legislature after those decisions and it must be presumed knowing of them, passed the Act of 1875 in terms which they must have contemplated would be decided in accordance with those decisions. Even, therefore, independently of “*Pain v. Boughtwood*,” it would have been held that the defendant ought to have been convicted. Appeal allowed, and case sent back to the magistrate with that intimation.

#### CORRESPONDENCE.

Dr. Van Hamel Roos (editor of the *Revue Internationale des Falsifications*) writes us, with reference to the note appended to the abstract appearing on page 195, Vol. xvi. of THE ANALYST, that there is now in the market a varnish for the purpose of protecting tin vessels quite different in composition to any hitherto used, and which, from a number of his own analyses, he finds entirely free from lead. By an improved process, the whole interior of the vessel is coated in such a manner that the food does not come in contact with the solder, absolute protection being thereby ensured.

# THE ANALYST.

FEBRUARY, 1892.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE ANNUAL MEETING of the Society of Public Analysts was held on the 6th January 1892, the President being in the chair.

The minutes of the last meeting were read and confirmed.

In the absence of the Treasurer, Mr. Dyer submitted the Balance Sheet for the year 1891, which was, upon the motion of Mr. F. H. Perry Coste, seconded by Mr. Bertram Blount, unanimously adopted.

*The President* (Mr. Otto Hehner) then read his Annual Address as follows :—

GENTLEMEN,

For many years past, my predecessors in this chair have, on the occasion of the Annual Meeting of the Society of Public Analysts, been able to speak of its flourishing condition and its progress. I am happy to-day to be in the same fortunate position, the year 1891 having been a satisfactory one in every respect.

We have elected nine new members and two associates, whilst we have lost by death, by resignation, and by removal, one member each, and by resignation two associates, so that we had on our lists on January 1st, 1892, 9 honorary and 172 ordinary members, and 23 associates—a total of 203.

The member taken by death during 1891 was not personally known to me, or, I believe, to any of us—Mr. Ernest Francis, of the Government Laboratory, Georgetown, Demerara. He had been a member for a considerable number of years.

On the second day of January of this year our Society lost one of its most esteemed members—Mr. Charles Heisch—the tidings of whose death will be received with sorrow by all chemists throughout the country. Mr. Heisch was one of the few surviving founders of the Chemical Society, and one of the fathers of the Society of Public Analysts. With the late Mr. Wigner he piloted it through its early stages, which, I need not remind you, were beset with many difficulties. For six years he filled the post

of Secretary, and for two that of President of the Society of Public Analysts, and it will always be remembered how faithfully he devoted himself to the advancement of the interests of Public Analysts. In his old age he was as clear-minded and energetic as the youngest of us, and ever kept abreast of the science which we represent. We all admired and loved the genial man, who to the very last retained a warm heart and a youthful spirit. His memory will be always dear to us.

Our balance-sheet shows this year an apparent reduction in our funds, for while last year we possessed about £323 we have at the present time only about £232, the difference being accounted for by the fact that from July 1st, 1891, the Society acquired the property of THE ANALYST Journal for the sum of £126. Allowing for this as an asset, our balance is the better by £35, to which must be added the sum of about £20, which we have to our credit on THE ANALYST account, so that, compared with last year, we are the richer this year by about £55.

The purchase of THE ANALYST has been an event of the greatest importance for the Society. You are all aware that THE ANALYST was started and originally owned by the Society. In the early years of our history, unfortunately, the funds were found inadequate to maintain a Journal, and it passed for that reason into the hands of Messrs. Wigner and Muter, and after the death of Mr. Wigner into those of Dr. Muter, who for many years maintained THE ANALYST by his own efforts, aided by an annual subsidy from the Society. When in the course of following years our financial condition improved, it was felt that the original intention of the founders of THE ANALYST, that is to say, of the Council of 1877, should be carried out. We have accordingly, as I have stated, and as is well known to all of you, re-purchased the copyright of the Journal. The time which has since elapsed is too short to allow of any conclusion being drawn as to the financial results of this step, although there cannot be the slightest doubt that it will prove a satisfactory one in every way. We have taken over THE ANALYST in the middle of a year, and have not, therefore, had the benefit of the bulk of the subscriptions, which become due at the beginning of each year; nor can there have been as yet any appreciable effect upon the circulation of the paper, which, it is hoped, will attend upon the efforts of the committee to make THE ANALYST a faithful and rapid record of the advance of all branches of Analytical Chemistry.

The present Editorial Committee have always had a superabundance of matter for insertion in the journal; indeed, the time is rapidly approaching when the enlargement of the paper will be unavoidable. Analytical chemistry throughout the world has, during the last few years, shown signs of great activity. In Germany and America several new and excellent Journals have been started, entirely or mainly devoted to analytical chemistry. The time when every chemist rushed into the field of exploration of new organic compounds—this fascinating pursuit, which for years has absorbed almost exclusively the attention of chemists—seems to near its end, and a due share of attention is again directed, as in the days of Berzelius, Liebig, Rose and Fresenius, to the necessary and careful analytical study of the innumerable compounds with which we are now

acquainted. This study has been far too long neglected. And if this country is not to remain behind in the race after new and applied knowledge, a good Analytical Journal is an absolute necessity. Not only Public Analysts are in need of it, but every technical and analytical chemist, and, not least, every manufacturer. THE ANALYST ought to fill, and surely will fill, that want. Analytical information is at present scattered piecemeal in the *Journal of the Chemical Society*, in that of the *Society of Chemical Industry*, in the *Chemical News*, and one or two other papers, but there is not published in this country any journal which collects all news of valuable analytical methods and advancements such as does, and has done for nearly thirty years, the *Zeitschrift fuer Analytische Chemie*, published by R. Fresenius. THE ANALYST ought to fill this position in the English language, and the efforts of the Society should be directed to that end.

Twenty-five papers were read before the Society in the course of last year. I give, in accordance with previous custom, a list of these :—

A Comparison of English and American Cider, by G. EMBREY.

On the Composition of Milk and Milk-products, DR. VIETH.

Remarks on the Analysis and Composition of Butter-fat, O. HEHNER.

On Malt Vinegar, O. HEHNER.

Some further points in the Detection of Adulteration of Vinegar, DR. W. J. SYKES.

A Method of detecting Butter mixed with Cocoa-nut Fat, DR. J. MUTER.

On measuring Milk for Quantitative Analysis, DR. P. VIETH.

Extraction of Fat from Milk-solids, A. W. STOKES.

On the Examination of Spirituous Liquids for Secondary Constituents, A. H. ALLEN  
and W. CHATTAWAY.

On the Action of Milk-preservatives, A. W. STOKES.

On the Influence of Boric Acid on Peptic Digestion, O. HEHNER.

Note on the Composition of Butter-fat, A. H. ALLEN.

Fat-free Paper for use in Milk-analysis, P. VIETH.

Fat-Extraction and Fat-calculation in Milk-analysis, P. VIETH.

Note on Tabarie's Process for the Indirect Determination of Alcohol T. B. BLUNT.

On the Determination of Alcohol by Tabarie's Method, A. H. ALLEN.

On the Adulteration of White Pepper, W. F. K. STOCK.

Note on the Schmid process, A. W. STOKES.

Notes from the Khedivial Laboratory, Cairo, H. D. RICHMOND.

Note on Tabarie's Process, SIDNEY HARVEY.

On Boracic Acid and Borax in Milk and Butter, W. W. FISHER.

Note on the Adulteration of Basic Slag, B. DYER.

On Gamoose-butter, H. D. RICHMOND.

Fat Extraction and Fat Calculation in Milk Analysis, H. D. RICHMOND.

Sixteen years have now elapsed since the Sale of Food and Drugs Act came into force, and since, with the creation of the Public Analyst, as we know him to-day, systematic analyses of articles of food, drink, and drugs, were undertaken. These sixteen

years have been an almost uninterrupted struggle with adverse circumstances. Methods of analyses had to be newly devised or improved; the composition of all articles of food had to be studied with far greater precision than before; experience had to be gained; analysts had to be educated; an intricate Act of Parliament had to be understood, and to be made workable; the public had to be taught to place confidence in the newly-created body of men; dealers had to be convinced of the honesty and capacity of the officers under the Act; unwilling justices of the peace, magistrates, and county councillors had to be brought to see that the Food Act was one of the most important they would have to administer to the bodily and material welfare of the people. Not one of these points has been finally reached, but steady progress has at least been made.

As to the education of Public Analysts, this Society by its meetings and by *THE ANALYST* Journal has accomplished much; far more than the most sanguine could have hoped fifteen years ago. It must be admitted, as it always freely has been admitted, that when the Act came into force, and men had to be appointed Public Analysts, here and there an incompetent one crept into the ranks; but at the present time no large district or important borough, at least, is without an Analyst, whose work and capacity is not only creditable to himself but also to his appointing authority. In a few smaller boroughs, in which the Act is barely in operation, there may survive a few remnants of a bygone age; may be a medical officer, who unwillingly accepted the post of Public Analyst because it was compulsorily coupled by short-sighted vestrymen with the post for which he was trained and which he fills worthily—that of sanitary officer. We may confidently look forward to the time when even these few will have made room for Analysts, who are Analysts by profession and study, and not by compulsion.

The public have never taken kindly to the Food Act, and have not mastered its details and intricacies. Probably they never will, but, on the whole, I think they look thankfully upon us as a body.

The trade in articles of food—and I take this to be a most satisfactory position to have attained—have, to a very great extent, abandoned their loudly-expressed hatred and contempt for Public Analysts. The trade-papers no longer teem with flouts and jibes at our expense, for the honest dealers—and the vast bulk of traders *are* honest—have recognised that even if the Act often times cuts hard against a man who has not the remotest intention to defraud, and yet found tripping, is brought before a magistrate as a malefactor, is held up to public opprobrium and fined—that in spite of such cases of hardship, which are due to the Act itself—the Public Analysts are their best friends, without whom honest and legitimate trade could hardly be carried on. A single dishonest dealer, if he were undisturbed, could by underselling, based upon adulteration, and upon fraud, disturb the equilibrium of a whole town, or even of a whole district, forcing competitors against their own will and desire into similar practices, if they wished to live. A butter-factor—such is a case in my own recent experience—who stoops to skilfully adulterate his butter with a moderate, yet paying percentage of margarine, so that he can undersell his honest

neighbours, can for a time compel a whole country-side to follow suit, with the disastrous consequence that the produce of a whole country may temporarily come into discredit. This happened last year in Belgium, whence for a time not a pound of butter was imported into England; and this year again, only a few weeks ago, in Italy, with almost equally disastrous results. Milk-dealers, again, now see in the analyst their friend, where fifteen and even ten years ago they thought they beheld their worst enemy.

Yet the Act, as I have said, often presses hard upon honest vendors. Articles of food pass through many hands before they reach the public or, may be, the inspector under the Act, and through him the analyst; the last link of the chain, the retailer, has to pay for the sins of all others, be these his shop assistants, the wholesale dealer, importer, factor or producer. A butter-man cannot have everyone of his consignments analysed, nor can every churn of milk be examined before it is sold. A warranty, in the absence of an analysis, is no protection, at least for the wholesale house or the importer, for these are often cheated in spite of the warranty, by the foreign shippers, who cannot be reached by the Food Act at all, but only by other legal proceedings, and then very rarely and after much litigation and expense. Over and over again have I seen dealers fined, or have been instrumental in getting them fined, who, I verily believe, were as honest as I hope I am myself. And yet I see no remedy for this. Certainly the stupid practice of many magistrates to let them off with a penny fine, is no remedy, but rather a crime against the public, who must, in the first instance, be protected in an effectual manner against fraud, intentional or unintentional. Only repeated hard cases can bring us into the way a real remedy. A warrant given by a wholesale house should always protect the retailer, but a warranty from one wholesale house to another, or from a foreign shipper to a wholesale dealer in England, should not protect, because the large dealer can either keep his own analyst or cause effectual chemical supervision to be made in a systematic manner, thus practically excluding deception.

At the present time, I regret to say, the main obstacles to the full carrying out of the Food Act are magistrates, and especially London magistrates. To read of penny fines inflicted for a gross deception of the public; to see excuses admitted, with magisterial benevolence, as must be uttered by offenders with tongue in cheek; to hear of cases dismissed because two analysts cannot agree within one or two units per cent. in their opinion as to the quantity of the adulterant, though both agree to the fact of adulteration, is, I again say, a fraud upon the public.

In spite of such obstacles the effects of the Act have been nothing short of startling, and have resulted in the saving of hundreds of thousands, nay, millions, of pounds of the public money. In the five years, 1877-81, the percentage of samples found adulterated in the whole of England and Wales was 16·2, from which figure it has regularly and steadily declined to 11·2 in 1890; that is to say, in fifteen years a reduction of 31 per cent. of the total adulteration. 27,465 samples were analysed during 1890, of which 3,069 were reported to be adulterated. Considering these large figures the unbiassed observer must admit that the Act has worked with very little friction indeed. But rarely

is a case of disputed analysis heard of nowadays, and references to Somerset House, with results contradictory to those obtained by the Public Analyst, are getting yearly fewer. Analysts have learnt their work and our referees, Somerset House, have likewise profited by the education afforded by this Society. From out of so large a number of cases of reported adulteration there will and must always arise a few cases of dispute, nay, there will ever be a few mistakes, for Public Analysts are no more infallible than are judges, whose judgments are reversed on appeal to higher courts. As a body, we can proudly say that our work is well and efficiently done, and can challenge comparison and enquiry.

The effect of the Act depends upon two factors. First, the vigilance and capacity of Public Analysts to be ready to cope with the newest forms of adulteration, for it cannot be denied that as we advance in knowledge, and give the results of our experience to our fellow analysts by the medium of our Journal, professional sophisticators are not slow to learn from us, and use the knowledge we acquire to defeat our own efforts. The milk trade has long ago learnt that, owing to the fluctuation in the composition of natural milk, they can water good, rich milk to some extent, without much risk of detection. Indeed, a milkman once admitted to me that he had only added to a particular sample "the *legal* quantity of water," namely, a pint to a gallon. In the butter trade, likewise, I am convinced from extensive experience, admixture with margarine is practised, chiefly in France and Belgium, upon the basis of previous analysis, made with the object to ascertain how much each consignment will stand without overstepping the limits of insoluble fatty acids or of the Reichert test. In view of this experience it behoves us to consider whether it is wise to make analytical results so public that they are available to everyone; and whether, in many cases, it would not be better if methods of analysis were handed from analyst to analyst in a more private manner. I am persuaded that, in the end, the Public Analysts will cope with every, even the most scientific, form of adulteration; but until a full knowledge of the composition and analysis of articles of food is obtained, years must elapse, and in the meanwhile fraudulent manufacturers reap their harvest. As an illustration of this I need only recall the adulteration of lard with cotton-oil. It was only after this practice had been in use for a year or two, that our attention was directed to it, and proceedings taken with very satisfactory results. But when the silver test enabled us readily to discover cotton-oil, even in small quantities, it was found that by merely heating the oil in contact with air it lost its reducing powers.

The second factor which influences the success or failure of the Food Act is the activity of local authorities in availing themselves of its provisions. From the statistics published by the Local Government Board it is clearly seen that, generally, when but few samples are analysed in a district, the percentage of adulteration rises, while with the activity of the inspectors it falls, until it reaches what we may consider an irreducible minimum. This fact has been most clearly pointed out by my predecessor, Dr. M. A. Adams, in his admirable Report to the Kent County Council, dated October, 1891. In Somerset, in which county the Act has been most actively carried out, one sample was analysed in 1890 for every 379 inhabitants. The proportion of adulterated samples out

of every 100 analysed was as little as 3·6. In Gloucestershire one sample was analysed for every 770 inhabitants, and the percentage of adulterated samples was 6·2. In Bedfordshire one sample to 821 inhabitants with 7·1 as percentage of adulteration. In Hampshire one to 1,224 people with 12·2 per cent. of adulteration. In Derbyshire one to 3,164 with 17·1. Suffolk one to 4,199 with 17·6. Oxfordshire, which has the distinction of being at the bottom of the list, analysed one sample to 14,963, and had 41·7 per cent. of all articles analysed adulterated.

These figures convey, as plainly as figures can speak, the lesson that all advance in analytical knowledge is of no avail if authorities, for some reason or other, neglect to carry out the provisions of the Food and Drugs Act, while vigilance and activity all but stamp out adulteration.

It will be said that such energetic measures would cost the ratepayers a large sum of money. In the first place, I would reply to this: what if it cost a county even a thousand pounds a year to save a hundredfold that sum to its inhabitants in the course of a year? What can you do with the beggarly sums, which are devoted annually by most counties—the twenty pounds, or hundred pounds—which are now considered sufficient for the working of the Act? But, in the second place, I am strongly of opinion that the Act should, to a great extent, be self-supporting. The fines inflicted should be sufficient to cover the expenses; the fraudulent dealer should be made to pay for the protection of the honest ones. With penny fines this is not to be done, and magistrates must not assess the costs of analysis at 7s. 6d., when they really amount to half a guinea or a guinea, as happened quite lately in one of the districts for which I am Public Analyst.

It is well known that the fines inflicted under the Food Act are absurdly small, while for the same offence, when proceeded against under, say, the Trade Marks Act, substantial fines are inflicted. Quite lately, proceedings against a vendor of adulterated butter, under the Trade Marks Act, resulted in fines amounting to upwards of fifty pounds, whilst fifty pence would have been deemed excessive if the summons had been taken out under the Food Act.

In spite of all this, we Public Analysts can rest assured that we have done good work and have, on the whole, carried out the duties which we have undertaken to the immense benefit of the country. This must be recognised by the public sooner or later, but even if it were not, if ingratitude and ignorance should prevail, we shall continue in the path which we have mapped out for ourselves. Very much remains yet to be done, and we are not likely to have an idle time before us; problems are springing up at every hand; in fact, with advance of our knowledge we see, as is usual, how little we know, and many years must yet elapse before we can say that we have got a thorough knowledge of that great department of science—the science of the composition of food. It is all very well for an Act of Parliament to say "Let there be food analysts;" but only years of study, of patient work, of mutual aid and communication amongst Public Analysts, can produce what Parliament considered they could create in a day, namely, the ideal Public Analyst.



A vote of condolence with the widow of Mr. Heisch was, upon the motion of the President, unanimously passed.

*The President* reported that Dr. Vieth was about leaving London, he having accepted a post in the North of Germany. He (the President) said that in Dr. Vieth the Society would lose a valued member. Dr. Vieth had read a great many interesting papers before the Society, and had added considerably to their knowledge of milk analysis. He desired to state, on behalf of the Council, that Dr. Vieth would be proposed for election as an honorary member of the Society.

A vote of thanks to the President for his interesting address was moved by Dr. Sykes, and seconded by Mr. Cassal, who expressed a hope that the sentiments it contained would be propagated largely to the advantage of the profession.

The motion was put by Dr. Sykes and carried unanimously.

The following gentlemen were proposed:—As honorary member, Dr. P. Vieth. As members—Mr. J. C. Welch, Reading; Mr. George Pilkington, Manchester; Mr. Benedict Kitto, London. As associates—Mr. E. C. P. Barber, Leeds (assistant to Mr. Fairley); Mr. H. L. Haller, Hull (assistant to Mr. Baynes).

*The President* then declared that Messrs. James Nimmo and Samuel Rideal had been duly elected members of the Society, and Messrs. C. M. Caines and W. P. Skertchley, associates.

The scrutineers, after having examined the ballot papers, reported that the following gentlemen were elected officers for the ensuing year:—

*President*—Otto Hehner.

*Vice-Presidents* who have filled the office of President:—M. A. Adams, F.R.C.S.; A. H. Allen; A. Dupre, Ph.D., F.R.S.; Alfred Hill, M.B.; J. Muter, Ph.D., M.A., F.R.S.E. Who have not filled the office of President:—B. R. Tatlock, F.R.S.E.; S. Harvey; P. Vieth, Ph.D.

*Treasurer*—C. W. Heaton.

*Hon. Secretaries*—R. H. Davies; Bernard Dyer, B.Sc.

*Other Members of Council*—T. Fairley, F.R.S.E.; W. J. Sykes, M.D., D.P.H.; F. L. Teed, D.Sc.; E. W. Voelcker; C. R. A. Wright, D.Sc., F.R.S.

The names of those members whose term of office has not yet expired, and who consequently do not retire this year, are A. Ashby, M.B.; T. B. Blunt; Sir C. Cameron, M.D.; C. E. Cassal; G. Embrey; John Hughes; and T. Stevenson, M.D.

The following paper was then read by Mr. Vasey:—

### THE ANALYSIS OF PEPTONES.

By C. W. HEATON AND S. A. VASEY (Charing Cross Hospital).

It is well known that in the digestion of meat by acid pepsin several compounds are obtained, which, although similar in composition, are by no means identical in chemical properties or nutritive value. Our knowledge of these compounds has of late been considerably extended, and various methods for their quantitative estimation have been

devised. We have no new re-agent to suggest; but after careful trial of all the processes at present in use, we have found that by a combination of several of them the analysis may be simplified.

The substances to be determined may, for analytical purposes, be classified as follows:—

1. Water; ash; total nitrogen.
2. Matters extracted by absolute alcohol. Definite compounds for the most part; some nitrogenous, some non-nitrogenous. It has been shown by M. Denaeayer (*v. infra*) that one variety of gelatin present in peptones is soluble in alcohol.
3. Albumins:—coagulated and rendered permanently insoluble by heat or by strong alcohol.
4. Albumoses:—not coagulated by heat. Soluble in water. Precipitated by alcohol, cupric hydrate, phospho-tungstic acid, mercuric chloride and ammonium sulphate.
5. Peptones:—not coagulated by heat. Soluble in water. Precipitated by alcohol, phospho-tungstic acid and mercuric chloride, but not by cupric hydrate or ammonium sulphate.
6. Gelatins:—partly soluble in alcohol. Precipitated entirely and in all forms by phospho-tungstic acid and ammonium sulphate. Not precipitated by cupric hydrate or mercuric chloride.

It is well known that the nitrogen in proteids varies from 14·4 per cent. in chondrin to over 18 per cent. in gelatin. (*Beilstein* iii., 1292-4.) Following previous workers, we have assumed 15·8 per cent. of nitrogen, which gives as the factor to be applied to the nitrogen 6·33. More exact knowledge is required before separate factors for each of the nitrogen determinations can safely be adopted.

The following is an abstract of the analytical methods described in recent researches from which our modified process has been derived:—

1. A. Stutzer (*Ber.* 13-251. *Ch. Soc. Absts.* 1880-676. *Cent. f. alleg. gesund. pflege*, 1882, 179. *Repert. Analy. Chem.* 1882-161. *Ch. Soc. Absts.* 1882-1239. ANALYST x. 57.)

Meat preparations are digested with pepsin in the usual manner. In the undissolved residue nitrogen is determined by soda-lime. The fluid is then agitated with cupric hydrate, suspended in weak glycerin, which, if the fluid be not too acid, throws down albumose. The separation appears to be complete, and the liquid filters well. In the cupric precipitate nitrogen is determined by soda-lime.

The cupric mixture can be prepared as follows:—

100 grammes of crystallized cupric sulphate are dissolved in 5 litres of water and 2·5 grammes of glycerin added. The solution is then made alkaline with caustic soda, and filtered. The precipitate is well mixed with a large excess of water containing 5 grammes of glycerin per litre. All traces of alkali are now completely removed by decantation and, if necessary, by filtration, the same glycerin solution being used throughout. The precipitate is then made up to 1 litre with water containing 10 per cent. of glycerin. The

thin emulsion then contains nearly 40 grammes per litre of cupric hydrate, and can easily be transferred by a pipette. It may conveniently be described as Stutzer's re-agent.

2. Kühne and Chittenden. (*Zeit. Biol.* xxii., 409, 423. *Ch. Soc. Abstr.* 1886, 818.)

The substance previously known as peptone was found to contain bodies of two kinds, one of which (albumose) can be precipitated and washed by a saturated solution of ammonium sulphate, while the other (peptone) remains in solution. The filtrate is concentrated until crystals of ammonium sulphate separate and the remaining sulphate is then removed by barium carbonate and hydrate, the excess of barium being carefully precipitated by sulphuric acid. Methods for the estimation of albumose and peptone are described. They involve the use of phospho-tungstic acid.

The paper contains much valuable matter in regard to the nature, composition and re-actions of peptones.

3. König and Kisch. (*Zeit. Analy. Chem.*, xxviii. 191. *Ch. Soc. Abs.* 1889, 803.)

The peptonic fluid is boiled and filtered. In the residue nitrogen is determined by the Kjeldahl process, and this multiplied by 6.25 gives albumen.

The filtrate is divided into two portions. In one, albumose only—as it was then thought—is thrown down and washed by ammonium sulphate, as in the method of Kühne and Chittenden, but the precipitate is treated differently.

It is weighed, and the ammonium sulphate in it is afterwards estimated volumetrically by barium chloride and deducted, the difference being taken as albumose. In the second portion both albumose and peptone are precipitated by phospho-tungstic acid. In the precipitate, nitrogen is estimated by the Kjeldahl process. Multiplying the nitrogen by 6.25, albumose and peptone are found, and so, of course, peptone by difference.

4. A. Denayer. (*Bull. de l'Assoc. Belge des Chimistes*, March, 1890. *ANALYST*, June, 1890.)

In this memoir it was shown that gelatin had been confounded with albumose in previous researches. Gelatin in all forms is precipitated by ammonium sulphate, so that the albumose found by the methods of Kühne and Chittenden and König and Kisch was really a mixture of albumose and gelatin. If albumin and albumose are previously separated, gelatin can be precipitated completely by ammonium sulphate. It is unnecessary to describe the analytical method founded on this important discovery, as it has been improved in a subsequent paper by the same author.

5. A. Denayer. (*Bull. de l'Assoc. Belge des Chimistes*, December, 1890. *ANALYST*, May, 1891.)

This memoir, recently translated and published with an addendum by Straker and Sons, London, contains later results of M. Denayer's work.

The analytical method which is described—although it is based upon those which preceded it—shows a distinct advance. Our own process is but a modification, and, we think, an improvement upon it. M. Denayer's system may be summarised as follows:—

(a) The peptonic fluid is treated with strong alcohol. After standing for 24 hours the precipitate, which consists of albumin, albumose, coagulable gelatin and

peptone, is washed with alcohol, dried and weighed. The solution is then divided into two portions, which are separately treated (*b* and *c*).

(*b*) One portion of the alcoholic solution is evaporated to dryness and extracted with warm water. Excess of saturated solution of ammonium sulphate is then added, and the mixture warmed. On cooling, the gelatin soluble in alcohol adheres to the basin, and may be washed slightly with ice-cold water, dried and weighed. It is then re-dissolved in warm water, and the ammonium sulphate in it estimated by barium chloride and deducted from the weighed gelatin.

(*c*) The second portion of the alcoholic solution is evaporated to dryness, dried over phosphoric anhydride for 8 hours and weighed. This operation is difficult as the residue is very hygroscopic, and M. Denaeÿer prefers to estimate the extractives approximately by difference.

The alcoholic precipitate is treated with warm water and filtered from albumin, which can be weighed in a tared filter. The solution is then divided into three portions.

(*d*) Of these, one is treated with excess of solution of phospho-tungstic acid.

This throws down albumose, gelatin and peptone. The precipitate is thrown on a tared Schleicher's filter, washed with dilute hydrochloric acid, dried and weighed. It is then burnt, and the proteids found by difference.

(*e*) Another portion of the aqueous solution of the alcoholic precipitate is treated with ammonium sulphate as in process (*b*).

The weight of the precipitate, after deducting the sulphate, gives albumose and gelatin.

(*f*) The third portion is accurately neutralised and treated with excess of saturated solution of mercuric chloride. This throws down albumose and peptone, but not gelatin. The precipitate is rejected. The filtrate is treated as before with ammonium sulphate, and the weight of gelatin insoluble in alcohol determined.\*

True peptone is now, of course, found by difference.

This scheme for the analysis of peptones is certainly the best that has hitherto been devised, but it is liable to objection in one or two respects. The process which we have adopted, and in which that of Stutzer is incorporated, appears to us simpler and more satisfactory.

6. A. Denaeÿer: (*Jour. Pharm. Anvers*, November, 1891. *ANALYST*, December, 1891.)†

This is an admirable process for a simple assay of genuine commercial peptones. 10 c.c. of aqueous peptone, containing about 2 grammes of dry matter, are treated with 100 c.c. of strong alcohol. After standing for 24 hours the precipitate is washed with alcohol, dried and weighed. The alcoholic solution is also dried at 105° C. and weighed.

\* In a subsequent note M. Denaeÿer recommends the removal of excess of mercury by H<sub>2</sub>S, and points out that the phospho-tungstic treatment may be avoided.

† Our paper was written before this note appeared.

M. Denaeyer holds that in a well-prepared peptone the alcohol extractive should not exceed 30 per cent., but we are inclined to think this too low an estimate. A large proportion indicates that leucine, tyrosine, and other products of metamorphosis are present. It is evident that this process is not intended to replace more exact methods of analysis. Its greatest defect is that, if gelatin had been added to the peptone, it would be precipitated by alcohol, and would, therefore, be weighed with the nutritive constituents.

#### THE MODIFIED PROCESS.

It is convenient to work with a tolerably concentrated solution. Any portion insoluble in warm, but not boiling water may be removed by filtration, and treated separately for nitrogen, &c. If a jelly be under examination it must be liquefied by heat or by dilution. In the following synopsis a strength of about 20 per cent. of solid matter is assumed. It is obvious that in any such scheme of analysis the mineral salts must be included among the organic proximate constituents, for our knowledge does not yet permit us to assign to albumose, peptone and the like, any definite proportion of mineral compounds. It is best to make separate estimations of water, ash and total nitrogen.

1. *Water; ash; total nitrogen.*—Estimated as usual. About 3 grammes for water and ash and about 1 gramme for total nitrogen, by the Kjeldahl method, are convenient quantities.

2. *Albumin; gelatin insoluble in alcohol (coagulable gelatin); albumose; peptone.*—40 grammes of fluid peptone containing about 80 per cent. of water are dropped gradually into 300 c.c. of nearly anhydrous alcohol, in a large weighed beaker and the mixture agitated by gentle centrifugal motion. After an hour or so the above-named compounds will have separated and can be washed with absolute alcohol by decantation. The alcoholic solution is preserved for further treatment and is hereafter alluded to as the *Stock alcoholic solution*. The beaker, with its contents, is then dried to constant weight at 100° C.

(a.) *Albumin.*—The weighed alcoholic precipitate is digested with warm water and washed on a tared filter. The residue, which has been rendered insoluble by the alcohol, is weighed as albumin.

The filtrate from albumin is diluted with water to 250 c.c. This may be described as the *Stock aqueous solution*.

(b.) *Albumose and gelatin.*—25 c.c. of stock aqueous solution are evaporated to a few c.c., treated with saturated solution of ammonium sulphate, raised to nearly 100° and quickly cooled with centrifugal agitation. The ppt. is thrown on a tared filter, washed with ammonium sulphate, dried and weighed. In the ppt. the excess of ammonium sulphate is afterwards estimated gravimetrically by barium chloride and deducted.

(c.) *Albumose.*—50 c.c. of stock aqueous solution are raised to near 100° C. and are then treated with 30 c.c. of Stutzer's reagent. The ppt. is washed in a filter with hot water and the nitrogen contained in it estimated by the Kjeldahl method. 30 c.c.  $\text{H}_2\text{SO}_4$  and a globule of mercury give good results.

(*d.*) *Gelatin*.—It is evident that from the results of the two last operations both gelatin and peptone may be found by difference, and our experiments convince us that a satisfactory assay may be obtained in this way. But a direct estimation of gelatin may be made as follows. The filtrate from the copper ppt. is concentrated to a few c.c., in a beaker previously weighed with a glass rod, saturated solution of ammonium sulphate is then added, the mixture raised nearly to the boiling point and then quickly cooled with centrifugal agitation. As M. Denaeayer has shown, the gelatin now separates and adheres to the sides and bottom of the beaker, particularly if touched from time to time with the rod. The gelatin may now be once washed rapidly with ice-cold water, dried and weighed and the ammonium sulphate retained in it estimated and deducted as before.

3. With regard to the alcoholic extract which we have described as the stock alcoholic solution, we confirm M. Denaeayer's statement that the dried extract is too hygroscopic to permit any accurate inference to be drawn from its weight. It is better to adopt the following method, which is in substantial agreement with that recommended by M. Denaeayer. The stock alcoholic solution is made up to a definite volume, say to 500, c.c. This is divided into fractions for separate treatment.

(*a.*) *Gelatin soluble in alcohol*.—One fraction, say 1-5th., is evaporated to dryness, taken up with warm water and treated with ammonium sulphate in the manner already described.

(*b.*) *Urea, &c.*—Another fraction, 1-10th., may be evaporated to dryness and treated with sodium hypobromite. But evidently the nitrogen could not with any accuracy be calculated as urea.

(*c.*) *Nitrogen*.—Another fraction, 1-5th., may be evaporated and treated by the Kjeldahl method for nitrogen. After deducting the nitrogen present as soluble gelatin, the residue multiplied by 3.12 gives the creatin-equivalent of crystallisable nitrogenous compounds.

(*d.*) *Ash in alcohol extractive*.—Another fraction may be used for the determination of ash.

The following analysis of a sample of beef-peptone prepared by M. Denaeayer will serve to illustrate the system.

The peptone was a semi-solid jelly, liquefied by gentle heat. It was sterile and bright, and was free from bitterness. It tasted like beef-tea and mixed easily with water.

## I.

|                 |     |     |     |     |     |              |
|-----------------|-----|-----|-----|-----|-----|--------------|
| Organic matters | ... | ... | ... | ... | ... | 15.59        |
| Mineral matters | ... | ... | ... | ... | ... | 2.43         |
| Water           | ... | ... | ... | ... | ... | 31.98        |
|                 |     |     |     |     |     | <hr/> 100.00 |

## II.

|  |      |      |        |
|--|------|------|--------|
| Albumins coagulated by heat and alcohol  | ...  | ...  | 0.12   |
| Matters precipitated by alcohol :—   |      |      |        |
| Gelatin (direct weighing)  | ...  | ...  | 2.00   |
| Albumose (Am. sulphate ppt. <i>minus</i> gelatin)                              | 5.06 |      |        |
| [N.B.] Albumose found by estimation of N. in Cu. ppt. $.79 \times 6.33 = 5.00$ |      |      |        |
| Peptone (difference)   | ...  | ...  | 3.33   |
| Total (direct weighing)  | ...  | ...  | 10.39  |
| Matters not precipitated by alcohol :—   |      |      |        |
| Gelatin soluble in alcohol (direct weighing)                                   | ...  | 1.30 |        |
| Extractive, &c. (difference)   | ...  | 6.21 |        |
| Total  | ...  | ...  | 7.51   |
| Water  | ...  | ...  | 81.98  |
|  |      |      | 100.00 |

## III.

Nitrogen (Kjeldahl) :—

|                    |     |     |      |
|--------------------|-----|-----|------|
| Total              | ... | ... | 2.67 |
| In alcoholic ppt.  | ... | ... | 1.38 |
| In albumose...     | ... | ... | .79  |
| Liberated by NaBrO | ... | ... | .22  |

In the absence of the respective authors, the Secretary read the following papers :—

“ON BORACIC ACID AND BORAX IN MILK AND BUTTER,”

by W. W. FISHER, M.A., OXON.; and

## SUPPLEMENTARY NOTE ON THE ANALYSIS OF WHITE PEPPER.

By W. F. K. STOCK, F.C.S., F.I.C.

AT the reading of a previous paper on the Adulteration of White Pepper (*THE ANALYST*, vol. xvi., p. 224), some misapprehension appeared to arise in respect of the effect of “grading” white pepper. I stated (p. 226) that “by no process of grading can the normal relation of the ash constituents of the *kernels* be disturbed,” and this, judging from some remarks which afterwards fell from the President, seems to have been taken as meaning that white pepper could not be graded. That was evidently a mistake, for there are no fewer than six or eight “grades” of commercial ground white pepper, and the point which I especially wished to bring before the Society of Public Analysts was, not that grading could not be done, but that it could not increase the proportion of ash beyond certain limits, and, more particularly, that it could not account for the presence of an abnormal proportion of calcium compounds in the ash of pepper.

As a means of removing doubt, I have made some further experiments upon the subject, and the results recorded below appear to me to prove my point beyond question.

A large sample of good quality commercial "decorticated" peppercorns was purchased. It was found to be nearly free from husk, and to consist almost entirely of the kernels.

These peppercorns were carefully ground and "graded" in the Laboratory, and they yielded the following percentage proportions:—

|       |  |     |     |        |
|-------|--|-----|-----|--------|
| No. 1 | Grains exceeding 1/16th in. diameter         | ... | ... | 17.63  |
| No. 2 | „ between 1/16th in. and 1/36th in. diameter | ..  |     | 32.06  |
| No. 3 | „ „ 1/36th in. and 1/70th in.                | „   | ... | 26.76  |
| No. 4 | „ below 1/70th in. diameter                  | ... | ... | 23.55  |
|       |  |     |     | 100.00 |

No. 5. The same peppercorns ground but not graded.

The five samples thus got were analysed with the following results:—

| Determination.   | No. 1<br>Grade. | No. 2<br>Grade. | No. 3<br>Grade. | No. 4<br>Grade. | No. 5<br>Not Graded. |
|--|-----------------|-----------------|-----------------|-----------------|----------------------|
| Water ... ..   | 14.12           | 14.38           | 14.04           | 15.10           | 14.24                |
| Fibre ... ..   | .41             | .65             | .55             | .65             | .48                  |
| Ash ... ..   | 1.25            | 1.15            | 1.23            | 1.23            | 1.13                 |
| Lime in Pepper calculated to Carbonate ...                               | .29             | .32             | .30             | .39             | .32                  |
| Percentage Proportion of Lime to Ash in {<br>terms of Carbonate ... .. } | 23.5            | 27.9            | 24.3            | 31.7            | 28.3                 |

I claim that the constancy of the ash percentages in the above table prove my point conclusively. I may be met with the objection that there are marked discrepancies in the ratios of Lime to Ash in terms of Carbonate. I am quite willing to admit that there are discrepancies, but members of this Society will hardly need to be told that *pure* pepper seldom yields, by simple ignition, an equally pure ash. I have made no attempt to elaborate the experiments by freeing the ash from residual carbon, etc., preferring to work upon the simple lines laid down in the paper already contributed.

*The President* wished to take the opportunity of making an explanation. It would be remembered that some time ago Mr. Stock was good enough to write a paper on pepper. In the discussion which followed, he (Mr. Hehner) made what he then thought were some quite innocent remarks, referring the members to a paper which he had read about that time on the grading of peppers. Mr. Stock had asked him to remove the wrong impression which he thought his (Mr. Hehner's) remarks had created. He might without any hesitation say that the paper in question—an abstract of which had since appeared in *THE ANALYST*\*—referred to black peppers and not to white peppers, whilst

\* Volume xvi., p. 235.



Mr. Stock's remarks were entirely directed to white. He (Mr. Fehner) wished to congratulate himself and the Members of the Society that his few remarks had led Mr. Stock to further enlighten them on the subject.

The two following papers were read by the Secretary :—

#### NOTE UPON THE ESTIMATION OF MILK SUGAR IN MILK.

AUGUSTUS H. GILL, PH.D.

THE main difficulty in this determination, as ordinarily carried out, is in obtaining a filtrate sufficiently clear for titration : as prepared by the usual methods, it is opalescent, or even quite turbid, from the fat which passes through the filter.

It has been found that by making use of the well known property of aluminium hydrate to drag down precipitates, and by following the recommendations of Radliscu,\* regarding the amount of acid, intensity and duration of heating, all of which are of great influence in the rapidity and completeness of the curdling, that a clear filtrate is readily obtained.

The method is as follows : 25 c.c. of the milk are mixed with 15 c.c. "milk of alumina," and 0.5 c.c. of twenty-five per cent. acetic acid added, the mixture stirred and heated 5—7 minutes in a water bath, the temperature of which is 35° C. One hundred cubic centimeters of water are now added and the mixture is heated in boiling water, for ten minutes, with frequent stirring. It is thoroughly cooled under the tap, allowed to settle and decanted through a plaited filter (S. & S. 597), into the 500 c.c. graduated flask, being careful to bring as little precipitate upon the filter as possible. The operations of boiling and filtering are repeated three times and the filtrates made up to 500 c.c. It is then ready for titration by Fehling's solution in the usual way.

The "milk of alumina" is prepared by precipitating at the boiling temperature 125 grms. ammonia alum with ammonium hydrate, washing the precipitate by decantation and making it up to one litre.

The method has been in use by the students here for a year, and has given very satisfactory results.

MASS. INST. OF TECHNOLOGY, BOSTON, MASS., U.S.A.

LABORATORY OF SANITARY CHEMISTRY.

#### THE POSTAL TRANSMISSION OF SAMPLES.

BY ALFRED ASHBY, M.B.

ON the passing of the Sale of Food and Drugs Act, 1875, when the analyst did not reside within two miles of the residence of any person requiring an article to be analysed, it might be forwarded to him through the Post Office, *as a registered letter*, subject to any regulations which the Postmaster-General might make in reference to the carrying and delivery of such article.

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\* Mittheilungen a. d. pharm. Inst. u. Labor. d. Univ. Erlangen. Hilger, Heft III., pp. 93—112.

This was the only legal way of conveying a sample under the Act, otherwise than by direct delivery of it by the purchaser to the analyst.

The Postmaster-General issued the necessary regulations, and they were in force for some time, but were subsequently withdrawn, when samples were no longer permitted to be sent through the Post Office in the only manner permitted by the Act, consequently, for a considerable period, there was no legal way of conveying articles purchased under it, other than by actual delivery from the purchaser to the analyst.

Nevertheless, many continued to be sent through the Post Office, but without registration, and it was foreseen by some of us that, sooner or later, prosecutions would fail through the informal delivery of samples.

This event, I believe, has happened somewhere in the Isle of Wight.

The difficulty has now been removed by the eleventh section of the Post Office Act, 1891 (54 & 55 Vict., c. 46), which amends the Act of 1875 in the following terms:—"In section sixteen of the Sale of Food and Drugs Act, 1875, respecting an article forwarded to the analyst through the Post Office, the words 'registered parcel' shall be substituted for the words registered letter."

Now that parcels may be registered in the same way as letters there is no longer, by virtue of this amendment, any impediment to the transmission of articles to analysts through the Post Office, when that mode of delivery is authorised by the Act of 1875; and if any future prosecution should fall through, owing to informal delivery of the sample, it will be due entirely to the carelessness of the purchaser.

I think the importance of this amendment is sufficient to warrant my bringing it to the notice of all public analysts, so that if it has escaped the notice of any, they may at once take the steps necessary to ensure all samples being sent to them in a legal manner by the officers of the local authorities for whom they act.

*The President* thanked the meeting for the honour they had done him in electing him President. He might say that the last year had passed in a very pleasant manner, and he thought he was entitled to say that he had kept on friendly terms with every one of the members.

It was their duty to pass a vote of thanks to the Chemical Society for the permission which had been accorded them of holding their meetings in that room; he, therefore, as President, proposed that the Secretaries convey the thanks of the Society to the Chemical Society. The vote was passed with acclamation; and this terminated the proceedings of the Society.

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**The Recognition of Unorganised Ferments in Blood. R. Kobert.**  
(*Read at the 64th meeting of the Deutsch. Naturforsch. u. Aerzte. Through Chem. Zeit.*).—The recognition of easily decomposed poisons in blood (frequently necessary, both for physiological purposes and for those of medical jurisprudence), is often difficult, on account of the red blood corpuscles by putrefaction or other causes becoming converted into a tarry

mass which is troublesome to deal with chemically and is useless for physiological examination. The removal of this substance is usually effected by dilution and heating after the addition of acetic acid, or by precipitation by alcohol, by potassium ferrocyanide and acetic acid, or by uranium nitrate. In all these cases the serum albumen, the albuminous enzymes and tox-albumens are also precipitated, on which account the recognition and isolation of the last two classes of substances are impossible.

The precipitant proposed by the author is powdered zinc. This reagent has for the forensic chemist, who has usually to deal with old putrid samples of blood, the advantage that it effects almost complete deodorisation. The completeness of the precipitation is not affected by the age of the sample. The following precautions are necessary:—

1. Perfectly fresh blood, which is always alkaline, must be neutralised previous to the addition of the zinc. The same remark applies to blood taken from bodies some weeks after death, in which the formation of ammonia has occurred. The normal alkalinity of blood disappears in 1 or 2 days whether kept in contact with air or allowed to remain in the corpse; even in the living subject it decreases enormously in certain illnesses [notably in fever] and in these instances zinc can be added direct.

2. The blood must be free from methæmoglobin. If present, the blood must be allowed to stand unshaken and undiluted in a corked vessel until the last trace is gone. It is well known that this removal is effected spontaneously alike in the body as in the collecting vessel, frequently in as short a time as twenty-four hours, even when the quantity of methæmoglobin is considerable.

3. The blood must be diluted with water to three or four times its original bulk.

4. The powdered zinc must be perfectly pure; that is, consist wholly of zinc and zinc oxide.

5. The quantity of zinc must be from  $\frac{1}{4}$  to  $\frac{1}{2}$  of the original weight of the blood.

6. The mixture must be vigorously shaken for some time.

When these conditions are complied with, the separation of the colouring matter of the blood is almost always complete, so that on washing the precipitate on the filter-press or on the filter-pump with a large amount of water, nothing goes again into solution. The yellowish brown colouring matter present in some bloods, is, of course, not precipitated and goes into the filtrate. The filtrate only contains tangible quantities of zinc in those cases in which compounds of organic acids were present in the blood. In the absence of these, only traces of zinc are present as albuminate, the quantity of which is smaller the freer the powdered zinc was from zinc oxide. The only poisons likely to be present in the precipitate are hydrocyanic acid and carbonic oxide, the former of which can be extracted with alcohol and the latter removed by the aid of the air pump.

The filtrate is vastly more suitable for physiological and chemical examination than the original blood. For observing its physiological effect, a portion is treated with one drop of sodium sulphide solution, shaken, and filtered from the precipitate of zinc sulphide, and the filtrate free from both zinc and sodium sulphide injected into a test animal [a mouse or kitten]. Usually the original filtrate without previous removal of

zinc can be used equally well. The bacteria always present in putrid blood are almost completely retained in the precipitate. When the filtrate is required absolutely free from bacteria it can be passed through a Chamberland filter. Should the test animal show strong symptoms of poisoning a second portion of the original filtrate is freed from zinc and albuminous matter by the addition of a drop of a solution of potassium ferrocyanide and a little acetic acid, and a second test made. If no poisoning be then perceptible the first test animal can only have been affected by some albuminous substance, inasmuch as potassium ferrocyanide could not have precipitated any other poison, in a solution so diluted, except possibly a portion of the strychnine, if that alkaloid be present. The isolation of the poisonous albuminous substances can only be effected by precipitation of the chief portion of the filtrate with alcohol in the ordinary manner or by salting out with ammonium sulphate. Should the second test animal show symptoms of poisoning like the first, the poison cannot be of albuminous character or at least not of the usual kind precipitable by potassium ferrocyanide. The original filtrate is then freed from albuminous matter and examined for other poisons by Dragendorff's method, the task being lightened by the circumstance that scarcely any foreign matter can be present.

In order to prove the utility of the method, portions of blood of 30 to 50 c.c. were mixed with 0.5 to 1.0 mgm. of strychnine, atropine, sapotoxine, and cadaverine, and these poisons recognised and recovered without difficulty. The method was further tested in cases of poisoning with alcohol, sulphuric acid and acetic acid, and by its aid alkaloidal substances were detected in the blood of persons who had died of such complaints as meningitis, peritonitis, and scarlatina. The process is also available for the estimation of sugar in blood.

B. B.

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**Testing Ammonia Solution.** J. Hertkorn. (*Chem. Zeit.* 1891, xv, 1493.)—

The method of testing ammonia solution for the presence of ammonium carbonate prescribed by the German pharmacopœia, consists in mixing the liquid with an equal volume of lime-water which should produce only slight turbidity. The author finds, however, that the chief portion of the carbonic acid contaminating commercial ammonia is not present as ammonium carbonate, but is derived from the ammonium carbamate generally present, the deduction being based on the observation, that on heating the ammonia solution with lime-water, a much more copious precipitation is obtained than in the cold. According to this, a sample which complies with the ordinary test may be quite unfit for analytical purposes, such as the separation of metals of the ammonium sulphide group from the alkaline earths, the determination of carbonic acid in beer, aerated waters, koumiss, &c.

B. B.

**The Reactions of Salicylic Acid.** G. Kottmeyer. (*Pharm. Post*, 1891, xxiv, 751, through *Chem. Zeit.*)—According to Vortmann, neutral salicylates give no precipitate with barium chloride or calcium chloride, even on the addition of ammonia, or on heating, or when an equal bulk of alcohol is added. Contrary to these assertions

the author finds that a 20 per cent. solution of sodium salicylate gives an immediate precipitate on shaking with a strong solution of calcium chloride; a 10 per cent. solution also gives a precipitate when ammonia is added; even a 1 per cent. solution mixed with a few drops of strong calcium chloride solution gives a precipitate on adding a little ammonia and shaking or warming. A slight precipitate is produced when barium chloride is added to a 20 per cent. solution of sodium salicylate, and a turbidity when a 10 per cent. solution is used.

B. B.

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**The Detection of Turkish Essence of Geranium in Rose Oil.** G. Panajotow. (*Ber.* 1891, xxiv. 2700, through *Chem. Zeit.*)—The samples of rose oil from Southern Bulgaria and Turkey are often adulterated with Turkish essence of geranium. This may be detected by treating two or three drops of the suspected specimen with 2 c.c. of fuchsine solution, which give a blue colouration, if even only a small quantity of the adulterant be present. Pure samples give a red colouration, but only after about twenty-four hours. Another method consists in heating the sample in a watch-glass with strong sulphuric acid, dense white tarry smelling fumes being given off by essence of geranium, and a thick red-brown fluid being formed, which becomes turbid on the addition of 95 per cent. of alcohol, yellow flocks separating, and the solution first becoming red, and then turning yellow on standing. A pure sample thus treated gives a red-brown liquid, which dissolves, and becomes almost colourless on the addition of alcohol.

B. B.

**Alberti and Hempel's Method of Determining the Ash of Sugar.** (*J. Fabr. Sucre.* 1891, xxxii. 37.)—Sidersky objects to this method (which was described in *THE ANALYST* xvi., 220), on the ground that ignition with sand decomposes the nitrates present in cane-sugar, necessitating a separate determination of their quantity in order to obtain an accurate determination of the total amount of organic matter in the sample analysed, and doubts whether it will displace the conventional method. An editorial note is appended to the abstract of this paper appearing in the *Chemiker Zeitung* to the effect that the objection has weight chiefly in the case of French, and possibly Belgian, sugars which contain more nitrate than German and Austrian samples, and will be even in these of decreasing importance, as the mode of cultivation is improved, and further states that a change in the conventional method is both desirable and imminent.

B. B.

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**Alberti and Hempel's Method of Determining the Ash of Sugar.** (*J. D. Zuckerind.* 1891, xvi. 1285.)—Alberti and Hempel, replying to Sidersky's objection (see preceding abstract) to their method, state that they have not overlooked the decomposition of the nitrates by sand, but thought well to ignore the correction it strictly involves, when formulating their method. The platinum vessels used are not severely corroded, as was at first feared, and only need scouring or cleansing by fusion with soda, after they have been used some forty times.

B. B.

# THE ANALYST.

MARCH, 1892.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A MEETING of the Society was held on the 3rd February, the President being in the chair.

The minutes of the last meeting were read and confirmed.

Mr. W. Chattaway was proposed as a member, and Mr. J. S. S. Brame, Assistant to Mr. Embrey, was proposed by the Council as an associate.

The President had pleasure in announcing that the Library of the Chemical Society would be open until 9 o'clock on the evenings on which the Society met.

The following gentlemen were duly elected:—

As honorary member:—P. Vieth, Ph.D., F.I.C., F.C.S., Analytical Chemist.

As members:—Benedict Kitto, F.I.C., F.G.S., 30 & 31, St. Swithin's Lane, E.C., Public Analyst for Cornwall; George Pilkington, F.I.C., 28, Pall Mall, Manchester, Analytical and Consulting Chemist; S. A. Vasey, F.I.C., F.C.S., Arncliffe, Drayton Road, Leytonstone, Analytical Chemist; John Cuthbert Welch, F.C.S., The Brewery, Reading, Analytical and Consulting Chemist.

As associates:—E. C. P. Barber, 34, Mount Preston, Leeds, Assistant to Mr. Fairley; H. S. Haller, Royal Chambers, Scale Lane, Huli, Assistant to Mr. Baynes.

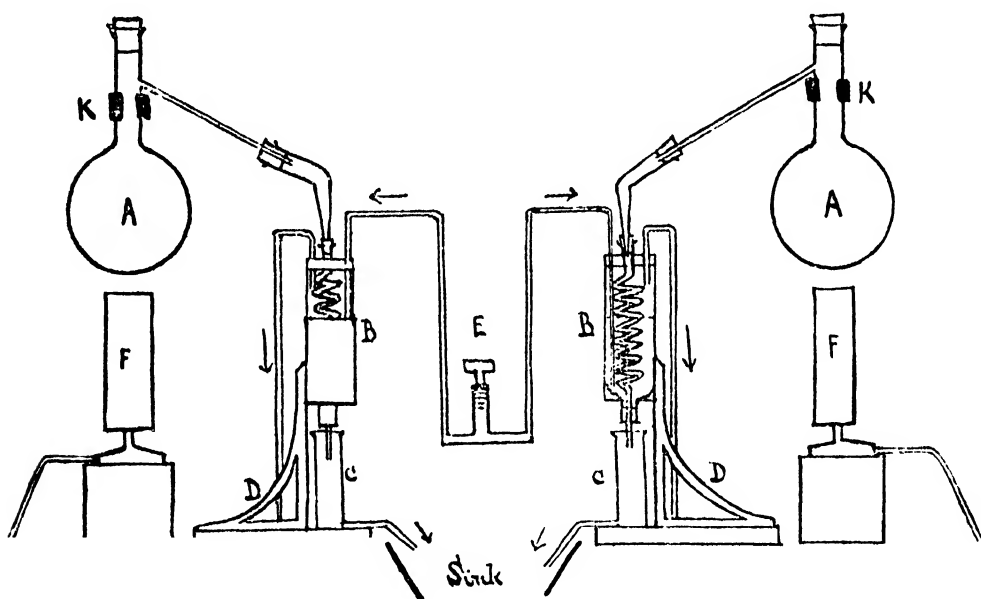
Mr. Embrey then read the following paper:—

## A CONVENIENT METHOD FOR ARRANGING THE APPARATUS USED IN DETERMINING FREE AND ALBUMINOID AMMONIA.

By G. EMBREY, F.C.S.

In the beginning of 1891, the citizens of Gloucester received the unwelcome news that the ordinary water supply was exhausted, and it became necessary at very short notice

to find some new ones. The river Severn at Gloucester is affected by the tide for about ten or twelve days during the month, and, as some seven or eight towns furnish it with a plentiful supply of sewage, there seemed only two sources: first, the Gloucester and Berkeley Ship Canal: and, second, numerous unused wells. Before sanctioning the use of these latter, it was thought by the authorities desirable to have an analysis made of each. Finding the ordinary clumsy arrangement of apparatus unsuitable, and having to make some twelve or more analyses each day, I set to work, with the help of a mechanically-inclined assistant, to devise an arrangement which I believe superior to that in common use; the ordinary clumsy retort and condenser takes up too much room and only one operation can be conveniently managed at one time. What I required was an arrangement so that two analyses could be kept going by one assistant.



My laboratory tables are 8 feet long, and 2 feet 3 inches wide, with a small sink with water tap in the middle. On each side of this sink was fitted a distilling flask with spiral condenser, the source of heat being an argand burner with iron chimney 8 inches high and 2 inches wide. As I had no room for retort stands, I contrived a simple clip screwed on to the shelf at back of bench; this keeps the table free for work. I find the burner can be turned up so that the flame reaches nearly to the top of the chimney, and there is no fear of cracking the flask; the water boiling in a few minutes, the condensation is far better than with the ordinary arrangement of straight Liebig condenser.

I find that by starting one analysis a little before the other, one assistant can perform two determinations in a little over an hour; so that myself and two assistants,

working eight hours, could make forty-eight determinations of free and albumenoid ammonia in one day. Though this speed was never reached, we came very near it. It will be noticed that a small convenient adaptor connects the flask with the condenser, the corks are covered with tin-foil, this being kept in place by a strong india rubber band. I would call attention to a convenient method of holding the spiral condenser: a small tin cup fastened to an iron bracket, this latter screwed to a wooden base with four screws at the corners, underside; this keeps it from moving about.

#### DESCRIPTION OF SKETCH SHOWING WATER APPARATUS.

- A A Distilling flasks.
- B B Spiral condensers.
- C C Nessler glasses.
- D D Brackets supporting condensers.
- E Water tap.
- F F Argand burners.
- K K Clips fastened to shelf.

#### DISCUSSION.

Mr. Cassal said that it had been his practice for many years to make use of a 40 to 45 ounce boiling flask for estimating ammonia in water analysis. He used a narrow glass condenser, 30 inches long, and of an inch internal diameter, with a straight condensing tube about 44 inches total length, but bent about 5 inches from the end, passing into the flask so as to give about 39 inches of straight length. The internal diameter of the condensing tube was half an inch. He preferred a straight condenser enclosed in a glass jacket, although he could well believe that Mr. Embrey's form of apparatus might be advantageous in small laboratories.

An important statement made by Mr. Embrey was that he obtained more perfect condensation with a spiral condenser, and could estimate saline ammonia which was not detectable by using the old form of apparatus. There was no doubt that the old metal condensers and accessory apparatus were cumbrous arrangements, devised rather for preventing satisfactory results than getting them.

Mr. Embrey in reply, said that the only point raised seemed to him to be the one of more perfect condensation. Everybody who had a large experience of Water Analysis with a straight condenser had seen steam at some time or other, in the early part of the process, issuing from the mouth of the straight condenser no matter how long the tube might be; this steam cannot be perfectly free from ammonia. In a spiral condenser there was the advantage that there was always a column of liquid present, and it seemed almost impossible for any steam to escape.

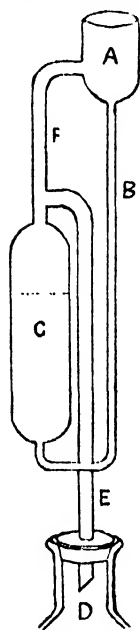


In the absence of the author, Mr. Dyer read the following paper :—

### A NEW FORM OF FAT-EXTRACTION APPARATUS FOR LIQUIDS.

By ALFRED SMETHAM, F.C.S., F.I.C.

SOME years ago I devised a form of fat-extraction apparatus for solids on the principle of upward filtration, but as it presented no advantages over the now well-known Soxhlet form I did not deem it desirable to publish an account of it. A few months ago, however, I had occasion to extract some liquids with ether, and it occurred to me that the apparatus might be pressed into service for that purpose; and as it answered all my expectations, I modified it somewhat in form and have now used it in my laboratory for some six months



or so. As it has been very serviceable to me, I venture to give a description of it to the Society in the hope that it may be useful to others—more particularly as it is specially adapted to the extraction of fat by the Schmid process.

The working of the apparatus will be easily understood by a glance at the accompanying diagram. The liquid to be extracted is poured into cup A so that the whole of it will run down the tube B into the bulb C, which should not be more than about two-thirds full. About 5 c.c. of ether are poured into a tared flask D, attached to the tube E by a cork in the usual way. The bulb C is then completely filled by adding ether carefully to the cup A, and the whole is adapted to an upright condenser—as with a Soxhlet tube. When the flask D is immersed in hot water, the ether vapour passes along the tubes E and F, is condensed in the Liebig's condenser and runs back by B into C, and rises drop by drop through the liquid to be extracted. The process is, therefore, continuous and automatic, and may be applied to any two non-miscible liquids, provided the solvent be the lighter.

To the Public Analyst it will, I apprehend, be chiefly of value because of its applicability to the extraction of fat from milk and its products; especially when treated by the Schmid process. For this purpose 10 c.c. of the sample under examination are measured or weighed into a little beaker, 10 c.c. of hydrochloric acid added, and the mixture gently boiled with constant stirring for two or three minutes. When cold, the mixture is poured into the apparatus as described and the beaker washed with ether and the washings added. The apparatus is then put together and the extraction allowed to proceed for an hour or so, when the whole of the fat will be found in the flask D. As there is only a small quantity of ether with the fat, the flask may be placed directly into the water-oven and the contents weighed to constancy in the usual way. The whole operation, so far as actual worth is concerned, can be performed very rapidly and with great ease and accuracy; the only error entering into the process being, so far as I have been able to ascertain, the slight solubility of some caramel-looking matter, which contaminates the fat to the extent of a milligram or two.

So far as my experience goes it appears that the extraction of the fat is more rapid

the more perfectly the milk and acid have been boiled together. Thus, when boiled for three minutes, practically the whole of the fat is removed in half an hour; whereas, when only boiled for two minutes, in one instance, 31 milligrams remained unextracted at the end of that time; while when boiled for one minute only about two-thirds of the total fat was extracted, the remainder being removed with difficulty. It would appear, therefore, that to readily extract the whole of the fat, it is necessary to boil the milk and acid together for some time, say three minutes.

The following results, obtained with four different samples of milk, and taken in this order, will give some idea of the accuracy of the process under varying conditions:—

|                         | Schmid,<br>Boiled with<br>HCl. for<br>1 minute | 2 minutes | 3 minutes<br>2.60 | 5 minutes | Adams method,<br>Extracted 3 hours |
|-------------------------|--|-----------|-------------------|-----------|------------------------------------|
| 1. Extracted 3 hours    |  |           |                   |           | 2.49                               |
| 2. „ $\frac{1}{2}$ hour |  | 3.91      | 4.49              |           |                                    |
| „ 1 „                   |  | 4.21      | 4.53              |           |                                    |
| „ $1\frac{1}{2}$ hours  |  | 4.46      | 4.56              |           | 4.51                               |
| 3. „ $\frac{1}{2}$ hour |  | 2.61      | 2.69              |           |                                    |
| „ 1 hour                |  | 2.75      | 2.75              |           |                                    |
| „ 2 hours               |  | 2.78      | 2.80              |           | 2.78                               |
| 4. „ $\frac{1}{2}$ hour | 2.31   |           |                   | 3.46      |                                    |
| „ 1 „                   | 3.33   |           |                   | 3.51      |                                    |
| „ $1\frac{1}{2}$ hours  | 3.49   |           |                   | 3.56      |                                    |
| „ $2\frac{1}{2}$ „      | 3.61   |           |                   |           | 3.57                               |

The determinations by the Adam's process were made by the use of Schleicher and Schüll's Fat-free paper, and the extraction was continued for three hours.

#### DISCUSSION.

Dr. Sykes pointed out that an apparatus with the same object had been recently described in "THE ANALYST," and which appeared to him to be much simpler and less fragile than the one described by Mr. Smetham. He also thought that Mr. Smetham's apparatus would be very difficult to clean, whereas the other one offered much less difficulty in this direction. The paper he alluded to was "On the Estimation of Mixtures of Saponifiable and Unsaponifiable Fats," by Hönig and Spitz, vol. xvi., p. 238.

Mr. Bernard Dyer would like to say that Mr. Smetham was perfectly aware of the existence of the apparatus referred to by Dr. Sykes; but Mr. Smetham's opinion was that his apparatus was simpler, better, and more workable. Messrs. Hönig and Spitz had happened, independently, to drop upon exactly the same principle.

The following paper was then read by the author:—

#### ON THE DRAWING UP OF CERTIFICATES.

By CHARLES E. CASSAL.

This concluded the proceedings of the Society.

## NOTES FROM THE KHEDIVAL LABORATORY, CAIRO.

By H. DROOP RICHMOND.

*Read at the Meeting, November 4th, 1891.*

4. **On Gamoose Butter.**—In the Journal of the Chemical Society, lvii., 757, in conjunction with A. Pappel, I gave figures of analysis of gamoose butter; the samples examined then were taken in the winter when, owing to the necessities of the country, the animals are exclusively stall-fed; I have now had the advantage of examining many samples of butter prepared in the summer months when, on the contrary, the animals are all out to pasture, and I find that important differences exist. The following are the chief figures obtained in the examination of these samples; for the sake of comparison the winter figures are added:—

|                                  |        | Summer.   |                     |     | Winter.                       |
|----------------------------------|--------|-----------|---------------------|-----|-------------------------------|
| Potash for saponification        | ... .. | 23·17     | ... ..              | ... | 22·04                         |
| Insoluble fatty acids            | ... .. | 86·9      | ... ..              | ... | 87·5                          |
| Of which (mean combining weight) |        | 265·0     | ... ..              | ... | 270·5                         |
| „ (Iodine Absorption)            | ... .. | 35·1      | ... ..              | ... | 41·8                          |
| Iodine Absorption                | ... .. | 32·0      | ... ..              | ... | 35·0                          |
| Soluble fatty acids (as butyric) | ... .. | 6·99      | ... ..              | ... | 6·09                          |
| Reichert-Wollny                  | ... .. | 34·7 c.c. | $\frac{N}{10}$ Alk. | ... | 25·4 c.c. $\frac{N}{10}$ Alk. |

The maxima and minima are respectively:—

|                           |        | Max.      |        |     | Min.       |
|---------------------------|--------|-----------|--------|-----|------------|
| Potash for saponification | ... .. | 23·33     | ... .. | ... | 22·86      |
| Insoluble Fatty Acids     | ... .. | 87·3      | ... .. | ... | 86·7       |
| Iodine Absorption         | ... .. | 32·5      | ... .. | ... | 31·6       |
| Reichert-Wollny           | ... .. | 39·0 c.c. | ... .. | ... | 30·65 c.c. |

Special attention was paid to the Reichert-Wollny determinations, this figure being taken for all samples which was not the case with the others. With regard to the sample giving 39·0 c.c. it was remarked that it was very liquid, and the portion fluid at 17° took 41·3 c.c.; on this being cooled to 0°, it did not completely solidify, and the liquid portion separated at that temperature took 45 c.c.  $\frac{N}{10}$  baryta solution to neutralise the volatile acids; the sample was then unfortunately too small to admit of the other properties being examined; this is probably the highest Reichert-Wollny figure obtained from a butter. With regard to this, it may be interesting here to record an experiment made some years ago in England. A butter which took 26·1 c.c.  $\frac{N}{10}$  R.-W. was melted and allowed to cool very slowly at about 25° C., being separated into portions, liquid and solid, which gave the following figures respectively:—

|                   |        | Solid.    |        |     | Liquid.   |
|-------------------|--------|-----------|--------|-----|-----------|
| Reichert-Wollny   | ... .. | 19·9 c.c. | ... .. | ... | 31·6 c.c. |
| Iodine Absorbed   | ... .. | 27·6      | ... .. | ... | 37·5      |
| Density at 15° C. | ... .. | —         | ... .. | ... | ·922      |

These figures show that the liquid portion contains not only more volatile acids, but

also more unsaturated acids; the density also is lower, Fleischmann (*Landwirth*, xxxiii., 251), giving the density of butter as .9307 on the average.

The great variations found have led me to search for indications of other methods of determining the purity of a butter than the usual determinations. I have long been of opinion that some regard should be paid to the ratio that the various figures bear to each other; this idea has been utilised by Muter (*ANALYST*, xv., 88), who proposes the ratio between the Reichert figure, and the index of refraction as given by Jean's oleo-refractometer as a means of detecting cocoa-nut oil. I have further developed this idea; from the absorption of potash, and the insoluble fatty acids (assuming that they have a constant mean combining weight), we can calculate the soluble fatty acids (as butyric), and assuming that a constant proportion of these passes into the distillate, we can calculate also the Reichert-Wollny figure; for the butter of the Gamoose, I take the following figures as the means for the combining weight, and the proportion of fatty acids distilling respectively 265 and 82 per cent., and using these I calculate the following formula:— $7.31 K - 1.55 I = R.-W. K = \text{Potash absorbed, } I = \text{Insoluble fatty acids and } R.-W. = \text{Reichert-Wollny figure.}$

This formula I have applied to the following samples with good results:—

| Insoluble Fatty Acids. | Potash Absorbed. | Reichert-Wollny found. | Calc. |
|------------------------|------------------|------------------------|-------|
| 87.5                   | 22.04            | 25.4                   | 25.5  |
| 87.15                  | 22.87            | 32.3                   | 32.1  |
| 86.9                   | 23.17            | 34.7                   | 34.7  |
| 86.7                   | 23.33            | 36.2                   | 36.15 |

Considering that the formula was obtained theoretically it is astonishing how close the results are, and although the number of samples is small, this agreement shows that there is a relation between the three figures. It is worthy of note that the summer and the winter butter, although very different in their figures, show that the same relation exists.

If now a butter be adulterated with cocoa-nut oil, this relation is changed, the calculated Reichert-Wollny figure coming out much too high, as in this oil only a very small portion of the soluble acids are volatile, certainly very much less than 82 per cent; the quantity of cocoa-nut oil may be calculated from the ratio of the difference between the calculated figure, and that found, to the difference between the calculated figure and 7 (the figure given on the average for cocoa-nut oil).

This equation does not apply to cows butter as is shown by the figures published by Allen (*ANALYST* xv., 4).

| Insoluble fatty acids. | Potash Absorbed. | R.-W. found. | R.-W. Calc. | Diff.  |
|------------------------|------------------|--------------|-------------|--------|
| 90.4                   | 22.16            | 22.5         | 21.9        | — .6   |
| 90.1                   | 22.09            | 24.55        | 21.9        | — 2.65 |
| 88.5                   | 22.67            | 29.2         | 28.3        | — .9   |

I have no other analysis at my disposal, but this discrepancy confirms the conclusion to which Pappel and I had arrived, that the Reichert-Wollny figure is low in Gamoose

butter as compared to the other figures; it will be interesting for any analysts, having samples of butter on which they have made the necessary determinations, to apply the formula with margarine; also the ratio is not the same as in butter, but the difference is so small that this method would not indicate such quantities as 10 per cent. or 20 per cent.

Another indication which I publish, in the hope that other chemists may verify or disprove the theory I have founded on it with European butters, has occurred to me from the following figures obtained from three butters, which were submitted to a fairly complete analysis :—

|                                      |     |     | 1     | 2     | 3     |
|--------------------------------------|-----|-----|-------|-------|-------|
| Mean combining weight of fatty acids | ... | ... | 264.0 | 265.7 | 270.5 |
| Iodine Absorption                    | „   | „   | 34.9  | 35.2  | 41.8  |

From these it is seen that the iodine absorption is increasing with the mean combining weight, indicating that the unsaturated acids have a higher mean combining weight than the saturated. From the average of these I calculate that .837 per cent. Iodine absorbed causes an increase in the mean combining weight of 1, and employing this figure, I calculate that the mean combining weight of the saturated fatty acids in 1, 2 and 3 respectively is 235.5, 236.2, and 234.8—average 235.5; and of the unsaturated acids 305.0, 305.0 and 303.6—average 304.5; these acids would absorb 83.2 per cent. of Iodine; with regard to this it is interesting to note that Pappel and myself (*loc. cit.*), found 297 as the mean combining weight of the unsaturated fatty acids of No. 3, and as the quantity operated on was less than half a gram., this number is in fairly satisfactory agreement with that calculated. I put forward this as it is not unreasonable to hope that the mean combining weight of the saturated fatty acids (at least), is sufficiently constant and sufficiently far removed from that of those of margarine, to be used as a means of discriminating between abnormal and adulterated butter; and I invite any chemists who have the time and the opportunity to make experiments, to determine whether this is the case with European butters; I regret that being in a far country I am unable to do this myself.

**5. Fat Extraction and Fat Calculation in Milk Analysis.**—In a paper published in THE ANALYST, xvii. 203, Dr. Vieth states that he is unable to accept my statement that the increasing difference between the paper and plaster methods as the amount of fat rises is only an apparent one, and does not accept my reasoning that, although the actual quantity is larger, it is a smaller proportion. As perhaps Dr. Vieth's opinion on this question is of more weight than that of any other analyst, I put forward more facts and arguments in support of my theory of milk extraction, hoping that by discussing the question fully we may arrive at a conclusion which can be accepted by both of us.

It behoves us first to consider what are actually the conditions when milk is dried up on paper and plaster respectively; taking, to begin with, the case of the paper, I cannot consider that paper is analogous in its action to that of a porous clay plate. I am of opinion that on filtering milk through filter paper, the filtrate is a watery solution of the solids not fat almost in their entirety together with .1 — .2 per cent fat, and that very

little of the casein remains with the fat. In support of this I quote the following determinations of the density of filtered milks, together with the solids not fat calculated therefrom by my formula; this last figure I correct by allowing for the loss of volume occupied by the fat, and on comparing this figure with the solids not fat actually found or calculated from the results of the analysis of the milk, it is seen that the agreement is very good indeed, and shows that very little of the casein is separated with the fat.

| No. | Density. | S.N.F. calc. | S.N.F. corr. | S.N.F.  | Of milk. | Diff. |
|-----|----------|--------------|--------------|---------|----------|-------|
|     |          |              |              | actual. | calc.    |       |
| 1.  | 1·0340   | 8·68         | 8·33         | 8·63    | 8·50     | — ·17 |
| 2.  | 1·0348   | 8·90         | 8·59         | 8·71    | 8·59     | —     |
| 3.  | 1·0345   | 8·80         | 8·49         | 8·63    | 8·62     | — ·13 |
| 4.  | 1·0326   | 8·31         | 7·96         | 8·18    | 8·20     | — ·24 |
| 5.  | 1·0331   | 8·45         | 8·27         | 8·36    | 8·33     | — ·06 |

The average difference between the solids not fat calculated from the filtered milk, and corrected, and the solids not fat calculated from the milk itself is — ·12 showing that very little of the casein separates with the fat. I have thought it just to take the calculated figure for comparison, as the error, due to the factors for the density of the solids not fat not being absolutely constant, is neutralised, and the figures are more strictly comparable.

I consider, then, that it is right to say that in the paper process the fat is practically separated, and the conditions of extraction are the most favourable.

To consider now the case of plaster; when milk is absorbed by plaster, it does not undergo this separation to the same extent, although doubtless partially, and consequently there is fat distributed among the particles of the plaster; when the plaster sets, it forms a mass impermeable or difficultly permeable to ether, and a portion of the fat is enclosed in a coating which prevents its extraction. What, then, is more reasonable to suppose than that in a milk containing a large quantity of fat a larger quantity, though perhaps a smaller proportion, owing to the more complete separation of the fat, is enclosed, and removed from the ether, than in a milk poor in fat? I attribute, then, the difference to the fact that setting the plaster imprisons some of the milk solids, and if the milk contains in one case a much larger quantity of fat than in the other, it is to my mind justifiable to expect that the enclosed milk solids should also contain a larger quantity of fat which is not extracted.

In the case of direct evaporation, it is the solids not fat themselves which imprison the fat, and a precisely similar explanation of this increasing difference applies.

I hope that Dr. Vieth will now be able to accept my theory, or if not that he will discuss still further this question, I being anxious to settle it, as I am of opinion that in science no fact should be lost, and no theory left unexplained, however unimportant they may seem at the moment, as we can never tell their future value.

I am extremely obliged personally to Dr. Vieth for having corrected the figures for the proportion of ash proteids and sugar in milk, as I had found in the milk of the Gamoose

that the proportion was almost exactly 1 : 5 : 6, and I was perplexed to find the reason why the solids not fat of Gamoose milk had a lower density in solution than those of cows' milk. Employing the figures given on p. 127 of THE ANALYST, vol. xiv., I calculate that for the proportion 1 : 5 : 6 the density should be 1.62, and for the proportion 2 : 9 : 13 it should be 1.635, while I actually find 1.589 for Gamoose milk, and 1.613 for cows' milk, a difference of .031 and .022 respectively; this shows that the factors used are probably not absolutely exact, but at the same time it confirms the conclusion I had arrived at that between Gamoose milk and cows' milk, there was very little difference as far as the density of the constituents was concerned.

**6. A Rapid Method of Milk Analysis.**--I have shown in the preceding note that on filtering milk, it is practically separated into a solution of solids not fat in water and fat; if the density of the milk be taken before and after filtration, the density of the milk after filtration less 1 divided by .004, very fairly represents the solids not fat, and the difference between the two divided by .0008, the fat.

| No. | Density.           |        | Diff. | S.N.F. |       | Fat.   |       |
|-----|--------------------|--------|-------|--------|-------|--------|-------|
|     | Before filtration. | After. |       | Found. | Calc. | Found. | Calc. |
| 1.  | 1.0308             | 1.0340 | .0032 | 8.63   | 8.50  | 3.94   | 4.0   |
| 2.  | 1.0318             | 1.0348 | .0030 | 8.71   | 8.70  | 3.35   | 3.75  |
| 3.  | 1.0316             | 1.0345 | .0029 | 8.63   | 8.63  | 3.61   | 3.62  |
| 4.  | 1.0298             | 1.0326 | .0028 | 8.18   | 8.15  | 3.80   | 3.5   |
| 5.  | 1.0315             | 1.0331 | .0016 | 8.36   | 8.27  | 1.99   | 2.0   |

Great exactitude cannot be expected, especially in the fat, but I think the figures quoted show that the method can be used by public analysts to sort out their milks.

#### DISCUSSION.

Dr. Vieth, in responding to the President's invitation, said that he felt that he was not acting altogether according to his own choice, but, so to speak, under compulsion, the paper being practically addressed to him. He wished first of all to thank the President for his kindness in giving him an opportunity of perusing the paper before it was read; and also to give expression to the pleasure with which he had listened to it. It was refreshing in our day to see an esteemed colleague exerting himself in the cause of truth solely for the sake of truth and science. In discussing the paper he felt he was working under two disadvantages; firstly, he had to do so in the absence of the author of the paper; and secondly, he could not expect that the majority of the Members of the Society should take a deep interest in a purely theoretical question of no practical consequence, and very little importance. He would try to be as brief as possible. Mr. Richmond, in the first part of his paper said that he could not consider paper analagous in its action to that of a porous clay plate. Perhaps it was not; but he questioned whether Mr. Richmond's filtration experiments proved that, what he had found, invariably took place when milk was put on filter or blotting paper. The filtration of milk was a thing which was much quicker said than done, and he did not think that Mr. Richmond wished them to understand that he had

accomplished the remarkable feat of practically separating milk by running it through a filter into milk serum and milk fat. He, Dr. Vieth, had made a filtration experiment with the following results: 200 c.c. of milk was poured on a plaited filter, after a lapse of one hour, 50 c.c. of the liquid had run through; after a further lapse of four and a-half hours, 26 c.c. were collected, and 108 c.c. were poured out of the filter. The four liquids were analysed and found to be composed as follows:—

|                | I.<br>Original<br>Milk. | II.<br>First<br>Filtrate. | III.<br>Second<br>Filtrate. | IV.<br>Milk left<br>on Filter. |
|----------------|-------------------------|---------------------------|-----------------------------|--------------------------------|
| Total Solids   | 13.42                   | 9.14                      | 8.14                        | 13.95                          |
| Fat            | 4.43                    | .06                       | .03                         | 4.80                           |
| Solids not Fat | 8.99                    | 9.08                      | 8.11                        | 9.15                           |
| Proteids       | 3.66                    | 3.68                      | 2.43                        | 3.89                           |

For every 100 parts of water there were present:—

|                |       |      |      |       |
|----------------|-------|------|------|-------|
| Solids not fat | 10.38 | 9.99 | 8.83 | 10.63 |
| Proteids       | 4.23  | 4.05 | 2.65 | 4.52  |

The differences in the liquids, II., III. and IV, as compared with the original milk were:—

|                |     |        |        |       |
|----------------|-----|--------|--------|-------|
| Solids not fat | ... | --0.39 | --1.55 | +0.25 |
| Proteids       | ... | --0.18 | --1.58 | +0.29 |

As he had made one experiment only, he did not feel justified in drawing final conclusions from it, nor did he wish that anyone else should do so. What he desired was that the results should induce Mr. Richmond to make further experiments in the same direction. No doubt the filtration could be accelerated by bringing the air-pump into requisition, but he should not expect that this would materially influence the composition of the filtrate. He could see three reasons which could account for the differences in Mr. Richmond's and his own results. Mr. Richmond might have worked on the very first portion of the filtrate, or he might have employed a totally different paper, or he might have experimented, not with cow's milk, but with the milk of the gamoose. Milk yielded by different kinds of animals, although apparently composed of the same constituent parts, undoubtedly showed some variations. Mr. Richmond himself had discovered a carbo-hydrate tewfikose in gamoose milk which was not identical with milk sugar. It was also known that whilst it was rather difficult to start alcoholic fermentation in cow's milk, mare's milk would ferment spontaneously. It was further known that there was considerable difference in the behaviour of the proteids present in cow's, mare's, and human milk, and also of the fats of the milk of different kinds of animals.

However, all this had very little to do with the point on which Mr. Richmond and himself differed. They were quite agreed that in the paper process, for the invention of which chemists were so much indebted to Mr. Adams, the conditions for extracting the fat were the most favourable, whatever they might be. Taking the paper process as a standard, it was found that the older methods failed to remove all the fat, or did so with



difficulty, and under certain conditions only. In the case of processes in which an inert substance was not employed, Mr. Richmond, in common with everybody else, was of opinion that the solids not fat imprisoned the fat, so that the solvent can only reach the latter with difficulty. In the case of the plaster process, there was, according to Mr. Richmond, an imprisoning action exercised by the setting plaster, which did not involve the fat alone, but all the milk solids. In Mr. Richmond's opinion, it was justifiable to expect that the more fat there was present, the larger would the amount imprisoned be, and he, Mr. Richmond, held that this explanation was good also in the case of the other obsolete methods. Mr. Richmond gave *one* explanation for *two* totally different facts. It was found in the processes worked without inert matter, that the differences, as compared with the paper process, increased with the increasing difficulties, *i. e.*, the poorer the milk was; but in the plaster process exactly the opposite was the case. He could not see that the plaster-setting-fat-imprisoning theory had brought the question nearer to solution. As he had mentioned already, the point was of no practical consequence, and of little importance, and he should leave the matter where it stood.

Mr. Richmond had alluded to the figures which he, Dr. Vieth, stated represented the proportions of ash, proteids, and sugar in milk. These figures could of course not, be taken as absolutely correct factors for all and every sample of milk. In the composition of the natural product of a living organism, infinite variations must be expected. Taking an average milk containing 8.8 per cent. of solids not fat, the figures formerly published and the figures corrected would give the following proportions:—

|          | 1 : 5 : 6 | 2 : 9 : 13 |
|----------|-----------|------------|
| Ash      | 0.73      | 0.73       |
| Proteids | 3.67      | 3.30       |
| Sugar    | 4.40      | 4.77       |

He believed that the latter figures were, in the majority of cases, nearer to the truth.

Many of the remarks made on the previous paper might be repeated with regard to Mr. Richmond's further paper. There was one point which he would like to draw special attention to, namely, that milks frequently looked fresh and unchanged, after they had developed an appreciable amount of acidity. Quite recently he had had to analyse a stale milk which appeared to be absolutely unchanged and did not curdle when heated to boiling. Nevertheless, when he had dealt with the sample for the fat extraction by the paper process, he could easily trace on the extracted coil the way in which he had run the pipette over the paper. It was marked out by a white line, or rather layer, which could be nothing else but casein.

**The Analysis of Sealing Wax.** C. Mangold. (*Zeit. angew. Chemie.*, 1892, p. 75).—Sealing wax consists chiefly of shellac and ordinary resin (colophony), to which such matters as chalk, magnesia, plaster of Paris, zinc white &c., are added for giving weight

and diminishing fusibility; also such substances as vermilion, red lead, ferric oxide, &c. for giving colour. The author proposes dissolving out the resinous portions with alcohol, and estimating the proportion of the two resins by the amount of iodine absorbed: the iodine number being approximately 115 for resin and 6 for shellac. He proceeds as follows: 5 grm. of the powdered sample are boiled on the water-bath with 150 c.c. of alcohol in a 250 c.c. flask, cooled, filled up to the mark, and allowed to settle completely. 50 c.c. of the clear fluid are pipetted off, and treated in the usual manner with Hübl's reagent. The undissolved portion is brought on to a tared filter, dried at 120° C., and weighed; the difference gives the amount of the resinous constituents. In an experiment, 5 grms. of sealing wax left 1.74 grms. of undissolved residue, equal to 34.8 per cent.; and hence contained 65.2 per cent. of resins. 50 c.c. of the alcoholic solution treated with Hübl's reagent absorbed 0.4309 gm. of iodine, consequently the iodine number was 66.1. The proportion of the resins was found by the following equation in which  $k$  = the amount of the colophony,  $s$  that of the shellac,  $s = 100 - k$ ,  $i = 66.1$ ,  $i' = 115$ ,  $i'' = 6$ ,

$$i = \frac{k i'}{100} + \frac{s i''}{100}, \text{ and } k = 100 \frac{i - i''}{i' - i''} = 55.1.$$

The resinous portion consists therefore of 55.1 per cent. colophony and 44.9 per cent. shellac; the sealing wax of 34.8 per cent. insoluble residue, 35.9 per cent. colophony, and 29.3 per cent. shellac.

W. J. S.

**Metal Vessels for Laboratory Use.** W. Dittmar. (*Chem. Zeit.* 1891, xv. 1521, and 1580-1589.)—(1.) *Copper Evaporating Dishes.* The advent of nickel as a laboratory material has caused the use of copper to be somewhat neglected; nevertheless its cheapness gives it the preference for many purposes, while for large vessels its relative permanency forbids its replacement by nickel-plated iron.

Besides the uses to which it is put in the pharmaceutical laboratory, it is well adapted for preparing baryta solution, and is, moreover, likely to be equally suited for the evaporation of many alkaline fluids, provided ammonia and cyanogen compounds are absent. It must be remembered that although copper is absolutely unattacked by water, the same cannot be said of it when tinned. This point will be referred to later.

(2.) *Globular Copper Flasks.*—The author has used copper flasks for years with success for the distillation of such liquids as alcohol, ether, and benzene, for distillations in a current of steam, and similar purposes. As a joint in such flasks is inevitable, their utility largely depends on the kind of solder used. For many purposes a soft soldered copper flask of about two litres capacity, which is sold in Glasgow as part of a coffee-making apparatus for about ten shillings, serves well. To avoid the presence of soft soldered joints, the author has had a flask of 6.5 litres capacity made of stout untinned copper, with brazed joints, and uses it with satisfaction for purifying and de-hydrating alcohol and ether. The method for the purification of the latter consists merely in keep-

ing the fluid to be de-hydrated over powdered caustic soda, for one or two weeks, in a flask of the kind described, and distilling on the water-bath, whereby a product is obtained, which has scarcely any perceptible action upon sodium.

Soft soldered copper flasks cannot conveniently be used for heating distilled water in place of glass flasks, (from which a certain amount of alkaline silicate is always dissolved) as lead is dissolved from the soldered joint; a copper flask soldered with silver solder is not open to this objection, and might moreover probably be used for caustic lye.

(3.) *Nickel Flasks*.—After several attempts, the author obtained two nickel flasks, soldered with silver solder, from the Westfälische Nickelwalzwerk, each having a capacity of 1.73 litres, and a weight of about 370 grms. The flasks were tested by boiling distilled water in them in free contact with air; in the water thus treated ammonium sulphide gave no precipitate. A second test was made by boiling a solution of 100 grms. of commercial caustic potash in 400 c.c. of distilled water under a vertical condenser, a portion of the liquid being then distilled off, and a sample of that remaining in the flask taken and tested for nickel. A trace of dissolved nickel was detected as soon as 100 c.c. had been distilled off, but a sample taken when 350 c.c. had been distilled off was free from nickel. An attempt was made to prepare caustic soda free from carbonate, by treating sodium carbonate with lime, and evaporating the clear liquid, by boiling it down briskly, in one of these nickel flasks, but without success, the product containing 0.96 of carbonic acid. A nickel flask of 800 c.c. capacity, obtained for the author by Baird and Tatlock, yielded a trace of metal in solution, on boiling with distilled water, apparently because it was brazed instead of being soldered with silver solder. Attention is called to the fact, that Fleitmann and Witte make sheet nickel, mechanically covered on both sides with platinum. This would be available for the construction of metallic laboratory vessels, although somewhat dear.

(4.) *Gold and Silver Vessels*.—The author has, in past years, made repeated attempts to obtain vessels unattacked by caustic alkalis. He points out that the current idea that gold and silver vessels are unaffected by caustic alkali is erroneous; it may be true for caustic soda but is absolutely false for caustic potash. The reason why the "Kalium hydricum purissimum" of Trommsdorff or Merck is quite white is that it contains more water than corresponds to the formula KOH. On attempting to de-hydrate it by fusion in a silver dish, oxygen is absorbed from the air, and silver from the dish immediately a certain point is passed; the material cannot therefore be at once anhydrous and pure. A similar result is obtained when gold, alloyed with 10 per cent. of silver is used, though a smaller quantity of water suffices to protect the metal from attack. Pure gold may do better; it is, however, doubtful. The purest caustic potash that the author was able to prepare, contained potassium carbonate and water, as well as a trace of gold (0.1 per cent.), sufficient to give it a dark brown colour. Laurent says "*La chimie est la science des corps qui n'existent pas,*" but the author hopes to give KOH a real existence

B. B.

**A Method for the Determination of the Specific Gravity of Powdered Substances.** W. J. Smeeth. (*Zeits. Krystall*, 1891, 483, through *Chem. Zeit.*)—Vaseline is placed in a small watch glass, warmed to expel air bubbles, cooled, and the whole weighed in water. The watch glass with the vaselene is then removed from the water, again warmed, and a weighed quantity of the powder, the specific gravity of which is to be determined, sprinkled upon it; after cooling and weighing again in water, the specific gravity can be found by an obvious calculation. B. B.

**The Determination of Cholesterin.** K. Obermuller. (*Zeits. Physiol. Chem.* xvi. 143, through *Chem. Zeit.*)—The first method proposed by the author depends on the method of saponifying fats by means of sodium ethylate, due to Kossel and Kruger (*THE ANALYST*, xvi., p. 178.) One gram. of the fat (*e.g.*, tallow filtered and dried at 120°C.) was, for the purpose of testing the method, mixed with a weighed quantity of cholesterin, dissolved in ether, and treated with sodium ethylate, produced by dissolving 0.15 gram. of sodium in the smallest possible quantity of 90 per cent. hot alcohol. The sodium ethylate is added to the ethereal fat solution and well shaken; saponification is complete after the mixture has been allowed to stand for three hours at the ordinary temperature. The quantity of alcohol used should not exceed 1 to 1.5 c.c.; the solution of the ethylate should solidify on cooling. The quantity of ether used must be sufficient to allow the soap formed to float freely in the liquid; about 80 c.c. is generally enough. After the mixture has been allowed to stand for three hours, the soap is transferred to a filter and washed with ether, which, if anhydrous, causes the precipitation of a further small quantity of soap, which is removed by a second filtration. The ethereal solution is then distilled, and the residue dried at 100 to 120°C. Purification is effected by treatment with a small quantity of absolute ether, the solution being allowed to stand for some hours and filtered from the small residue of soap; distillation, and drying as before, complete the process. The method only gives good results with solid fats.

The author describes another method in which the cholesterin, obtained as in the previous process, is dissolved in carbon disulphide, and titrated with a solution of bromine in the same solvent, until a yellowish-red colouration appears; the results were satisfactory. It is at present unknown how bromine behaves with bodies analogous to cholesterin; the author has found that ischolesterin, like cholesterin itself, combines with two atoms of bromine, but no figures have yet been recorded for phytosterin, caulosterin and ambrain.

B. B.

**Determination of Fat in Milk Products.** Leze and Allard. (*Compt. Rend.* cxiii. 654, through *Chem. Zeit.*)—The process depends upon the same principle as that of Schmid, in which the casein of milk is dissolved by heating with strong hydrochloric acid, but differs therefrom inasmuch as the acid is afterwards neutralised with ammonia,

warm water added, and the volume of the fat itself read off in the graduated neck of the flask in which the reaction is conducted. An improvement in this process has now been effected by allowing the hydrochloric acid to act for several hours at 25 to 30° C. The acid should be free from free chlorine, otherwise a flocculent precipitate forms, and an evolution of gas takes place, which make the measurement of the volume of fat difficult; the addition of ammonia may be omitted.

The process can be applied to the determination of fat in various milk products, such as cream and cheese, as well as in margarine. The substance to be examined is treated in a flask with a graduated neck, with 4 or 5 times its volume of pure concentrated hydrochloric acid, and allowed to remain for some time at a moderate temperature with frequent shaking. The substance dissolves to a clear brown liquid from which the fat separates; by the addition of warm water, the fat can be brought into the graduated neck and there measured. If the substance be troublesome to introduce into a flask, the treatment with acid may be carried out in a dish, and the resulting solution transferred to the graduated vessel. The author found in a sample of Gruyere, 31.75 per cent. of fat, against 31.84 per cent. by extraction with ether, and 32.04 by treatment with carbon disulphide. In this particular instance the reaction took place easily when 10 grms. of cheese were digested with 50 grms. of hydrochloric acid for about half-an-hour, and heated on the water-bath until the solution assumed a brown colour. The observed volume of fat can be calculated into grms. by multiplication by 0.9, or 9 grms. can be taken and the volume read off at once in percentages without correction. B. B.

**A Reaction of Cerous Oxide.** P. C. Plugge. (*Archiv. der Pharmacie*, cccxix 558-561).—In some pharmacopœias cerium oxalate has been incorporated among the remedies for vomiting, dyspepsia, and catarrh of the stomach and intestines, and the author has met with a case in which cerium oxalate occurred in the contents of a stomach submitted for analysis for poison. It thus becomes necessary to have a delicate test for cerium oxide; such is supplied by a solution of 1 part of strychnine in 1000 parts of strong sulphuric acid. A little of the solution supposed to contain cerium is made just alkaline with sodium hydroxide, evaporated to dryness on a piece of porcelain, and the residue mixed with 2 or 3 drops of the strychnine solution. A bright blue colour, which shortly gives way to a more permanent cherry-red or pale-red colour, is indicative of cerium. One-tenth of a milligram of cerous oxide will give the bright blue colour, while one hundredth of a milligram will give a pale and fugitive blue-violet colour, about which, however, there is no uncertainty.

Cerium oxalate will not give the reaction without the presence of sodium hydroxide. The test will answer in the presence of zinc and aluminium in a precipitate obtained by ammonia, but not if ammonium sulphide or zinc sulphide be present. A. G. B.

**Test for Phenacetin.** W. Autenrieth and O. Hinsberg. (*Archiv. der*

*Pharmacie*, cccxix., 456).—In a paper on the derivatives of phenacetin, the authors point out that phenacetin may be distinguished from its fellow antipyretics—antifebrin and antipyrin—by boiling the suspected substance with dilute nitric acid (10–12 per cent.) for a short time. Phenacetin is thus nitrated, and the nitro-derivative colours the nitric acid solution yellow or orange, whereas a similar solution of antifebrin and antipyrin remains colourless. When the yellow solution is cooled, the nitro-phenacetin crystallizes in yellow needles.

A. G. B.

**On the Estimation of Potassium as Perchlorate.** W. Wense. (*Zeitsch. f. angew. Chem.* 1891, p. 69.)—The perchlorate method has been generally abandoned on account of the solubility of the potassium salt in water or alcohol, one part of the salt requiring 6,400 parts of 97 per cent. alcohol, about 5,000 of 95·8 per cent., and 2,500 to 3,000 of 90 per cent. According to the author, a mixture of two parts by volume of 97 per cent. alcohol and one part of ether, dissolves only 1/25,000 part of potassium perchlorate. He further found that the solubility was much diminished in presence of perchloric acid, and of the sodium, magnesium, and barium salts of that acid. He therefore uses for the purpose of washing the precipitated potassium, perchlorate, alcohol to which a small quantity of perchloric acid has been added. He operates as follows:—The salts to be analysed must be free from sulphates and from non-volatile acids. He evaporates them with an excess of perchloric acid in a well-glazed china basin until no more hydrochloric or other acid vapours escape. To the residue about 10 c.c. of alcohol are added, containing 0·2 per cent. of perchloric acid, the precipitate is rubbed with a glass rod, the fluid poured upon a weighed filter, and the precipitate brought upon it with the acid alcohol mixture. It is then washed with a few c.c. of pure alcohol, and dried at from 120 to 130°C., one part of perchlorate corresponding to 0·5382 KCl, or 0·6289 K<sub>2</sub>SO<sub>4</sub>. A number of test experiments are given which are entirely satisfactory.

O. H.

**The Attack of Chrome Iron Ore by Hydrochloric Acid under Pressure.** P. Jannasch and H. Vogtherr. (*Ber.* xxiv. 3206–3208.)—The mineral can be attacked either in a tube of hard potash glass, if the content of chromium only be required, or in Jannasch's platinum apparatus (*Ber.* xxiv. 273), if a complete analysis be undertaken. The substance must be powdered with the same care as is exercised in the ordinary fusion methods of attack. About 1 grm. of the chrome iron ore is mixed with 2 grms. of ammonium chloride and 10 c.c. of hydrochloric acid (4 vols. of the acid of sp. gr. 1·119 and 1 vol. of water) saturated with ammonium chloride by shaking with excess of that salt and heated in a sealed tube for 8–10 hours at 275°–290°C. Test analyses, in which the insoluble residue left by this treatment was treated with hydrofluoric acid and sulphuric acid to remove silica, showed that the quantity of unattacked ore ranged from 0·17 per cent. to 1·22 per cent., the latter somewhat high figure being due to the imperfect pulverisation of the mineral.

B. B.

**The Quantitative Separation of Manganese and Nickel, Manganese and Cobalt, and of Manganese, Cobalt, and Nickel.** P. Jannasch and C. J. Franzek. (*Ber.* xxiv. 3204, 3205.)—One of the authors, in conjunction with Mac Gregory, some time ago published (*J. f. Prakt. Chem.* xliii. 402) a method of separating manganese and zinc by means of hydrogen peroxide in strongly ammoniacal solution in the presence of much ammonium chloride. The present coadjutors find that manganese and nickel can be separated in the same manner; they failed, however, in their attempt to apply the method to manganese and cobalt, the latter being carried down in considerable quantity and not being removeable even by repeated treatment. The object in view was eventually attained by using hydrogen peroxide as a precipitant in a solution of the double cyanides of the metals in the presence of potash. Under these conditions, the manganese is precipitated quite free from cobalt. The method is applicable to the case of nickel and manganese. The exact conditions necessary for success will be published in a later paper. B. B.

**The Micro-Chemical Detection of Sulphurous Acid.** G. Deniges. (*J. Ph. Chim.* 1891, xxiv. 289, through *Chem. Zeit.*)—The reactions generally in use for the detection of gaseous sulphurous acid do not suffice to discriminate between it and other reducing gases, notably sulphuretted hydrogen. The method used by the author consists in exposing a glass rod, wet with a mixture of chlorine water, hydrochloric acid, and barium chloride, to the suspected gas, and in recognising the crystals of barium sulphate, which are lozenged-shaped, and either isolated or united in cruciform groups, under the microscope. The absence of vapour of sulphuric acid is first ascertained by making a test with barium chloride solution acidulated with hydrochloric acid, in a precisely similar manner.

A second test is described, depending on the formation of one of the very sparingly soluble crystalline compounds of metallic sulphites with primary aromatic amines, already investigated by the author. A saturated solution of cadmium nitrate is diluted with twenty times its bulk of a solution of aniline, containing 20-25 grms. per litre. Just before being used, a small quantity of this mixed solution is treated with about 190 times its volume of acetic acid. A glass rod dipped in this mixture and exposed to an atmosphere containing sulphurous acid is speedily covered with a white film, which seen under the microscope consists of very regular hexagonal plates. When the reagent is not acidified, the reaction is more sensitive, the precipitate forming more rapidly; but the hexagonal plates are replaced by much less characteristic radial crystals. B. B.

**Metatitanic Acid and the Determination of Titanium by means of Hydrogen Peroxide.** F. P. Dunnington. (*J. Amer. Chem. Soc.* 1891, xiii. 210, through *Chem. Zeit.*)—The detection and determination of small quantities of titanate acid have

been facilitated by the method due to A. Weller, which depends upon the formation of an intense yellow colouration when hydrogen peroxide is added. Exact results are obtained if the product of the fusion of the titanac acid, to be determined with sodium bisulphate, is dissolved in sulphuric acid of not less than 5 per cent. strength; the results are low when the acid is weaker. A similar defect is observed when a weak acid solution of titanium sulphate is diluted, heated until partial precipitation has taken place, the precipitate re-dissolved in sulphuric acid, and hydrogen peroxide added. The author has found that these phenomena are due to the presence of metatitanic acid.

Metatitanic acid can be isolated by heating a dilute solution of titanium sulphate to 100°C., gradually adding ammonia in excess, filtering and warming the washed precipitate with hydrochloric acid, in which a portion remains almost insoluble. After washing once or twice by decantation with cold water, whereby most of the hydrochloric acid is removed, the residue is found to be completely and readily soluble in water. On treating the above-mentioned precipitate with hydrochloric acid and removing the latter by evaporation upon the water bath, a scaly residue is left of gelatinous aspect which gives an opaline solution in water, and contains one molecule of water to each molecule of titanac acid; thus having the same composition as that assigned by Merz to air-dried metatitanic acid. The aqueous solution of metatitanic acid gives a white precipitate with hydrogen peroxide instead of a yellow colouration. It therefore appears that after the fusion of titanac acid with sodium bisulphate and digestion with water only, the solution contains some metatitanic acid, which gives no yellow colouration with hydrogen peroxide; it is therefore necessary in using Weller's process to have sufficient sulphuric acid present to prevent the formation of a precipitate, even in warm solutions; 5 per cent. is enough for this purpose.

B. B.

**Detection of Vegetable Fatty Oils in Lard.** P. Welmans. (*Pharm. Zeit.* 1891, p. 798, through *Zeit. angewand. Chemie.*)—If 2 c.c. of phosphomolybdic acid are added to 1 gm. of a fatty oil dissolved in 5 c.c. of chloroform, and the mixture well shaken, it becomes of an emerald green color, owing to the reduction of the reagent. On standing the fluid separates into two layers, the lower chloroform one, which was originally of a yellow tint, is now colorless; the upper layer exhibits a beautiful green coloration. If the acid fluid be supersaturated with ammonia or other alkali, the green colour changes to a blue, corresponding in intensity to that of the original green colour. The reaction shows itself with nearly all vegetable fatty oils; those, which have been chemically treated, either for the purpose of being bleached or for the removal of acidity, do not respond to the test at all, or only in a feeble manner, and that after standing some time. Lard, goose fat, tallow, deer fat, butter fat, &c., show no change in colour, on being treated with this reagent either with or without the addition of alkali. The presence of a small quantity of vegetable fatty oil betrays itself by the appearance of the above mentioned coloration, the intensity of which forms an approximate measure of the quantity of vegetable oil present in the sample. In experiments with American lards,



which deviated in their iodine absorption numbers from that of genuine lard, the results were concordant, the color deepening as the iodine figure rose. The mineral fats (paraffin, vaseline), are without action on this reagent, and the only animal fat which reduces it is cod liver oil.

If to 10 c.c. of oil a cold saturated solution of picric acid in ether be added, and the latter be allowed to evaporate slowly away, the acid remains dissolved in the oil, to which it communicates a brown color. This reaction can be used for the detection of cotton seed oil in lard, which, when pure, after the ether has evaporated, appears of a citron yellow color; if, however, cotton seed be present, the mixture assumes a brown red color.

W. J. S.

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**The Essential Oil of Lemons. V. Oliveri.** (*Gaz. Chim., Italiana* 1891, 318.)—

The essential oil of lemons consists of about 60 per cent. of a limonene,  $C_{10}H_{16}$ , b. p.  $170^{\circ}$ — $170.5^{\circ}$ , density 0.8867,  $[\alpha]_D$   $64.82^{\circ}$ , forming a tetra-bromide and a di-chlorhydrate, about 90 per cent. of a limonene  $C_{10}H_{16}$ , b. p.  $176^{\circ}$ — $178^{\circ}$ , density .8990,  $[\alpha]_D$   $76.75^{\circ}$ , forming a tetra-bromide and a dichlorhydrate; both these limonenes give a red colour with sulphuric acid in acetic solution, and a small quantity of a sesqui-limonene  $C_{15}H_{24}$ , b. p.  $240^{\circ}$ — $242^{\circ}$ , density 0.9847, inactive, and forming a tetra-bromide and a dichlorhydrate. In acetic solution it gives a brown colour with sulphuric acid.

Essential oil of lemons is often adulterated with turpentine; this can be detected by the following properties; turpentine from the *Pinus Maritimus* (French turpentine) gives a mono-chlorhydrate containing 20 per cent. Cl against 33.97 per cent. in di-limonene-chlorhydrate; this method of detecting adulteration is scarcely practical, and the author bases his method of distinction on the specific rotary power; in ten samples he finds the density to vary from 0.856 to 0.865, and the rotation in a 200 m.m. tube from  $117^{\circ}$  to  $123.6^{\circ}$ , while French turpentine gives density 0.870 to 0.881, and rotation in 200 m.m. tube— $45.5^{\circ}$  to  $64.0^{\circ}$ ; Russian turpentine from *P. sylvestris* gives a rotation of about  $21^{\circ}$ , and American turpentine from *P. australis* about  $23^{\circ}$ .

Any rotation then of less than  $116^{\circ}$  should be considered as indicating adulteration.

H. D. R.

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OBITUARY.

The late Dr. A. J. BERNAYS.

We regret to have to announce the death of this gentleman, which took place on the 5th of January last. He was one of the earliest members of the Society of Public Analysts, and for some time a member of its Council. For thirty-one years Dr. Bernays was lecturer on Chemistry at St. Thomas's Hospital, having previously held a similar position at St. Mary's Hospital, and he was examiner in Chemistry to the Colleges of Physicians and Surgeons. As Public Analyst for St. Giles, Camberwell, and St. Saviour's, Southwark, he was intimately connected with the working of the Sale of Food and Drugs Act. His amiable manners, his modest and genial disposition, gained for him the esteem of all those with whom he was brought in contact

# THE ANALYST.

APRIL, 1892.

## THE LATE PROFESSOR REDWOOD.

We have to record with deep regret the death, on the 5th of last month, of the first President of the Society of Public Analysts, Dr. Theophilus Redwood, Public Analyst for the county of Middlesex, for the districts of Holborn and St. Giles, and for the borough of Luton. It is, however, in connection with Pharmacy that Professor Redwood's name will be longest remembered; he was one of the founders of the Pharmaceutical Society, and was intimately associated with it for a long period of years. He acted as Secretary to the Committee, appointed in 1854, to revise the London Pharmacopœia, and was personally entrusted by the Medical Council with the editing of the 1867 and two following editions of the British Pharmacopœia. In conjunction with Professors Graham and Hofmann, he was engaged by the Government to investigate the subject of fermentation; one result of their conjoint labors being the compilation of the Original Gravity Tables still in use. He was presented with the Degree of Ph.D. by the University of Giessen at the special request of Professor Liebig. On retiring from active life in 1855 he was appointed Emeritus Professor of the Pharmaceutical Society of Great Britain. Dr. Redwood had reached the age of eighty-six years.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A meeting of the Society was held on Wednesday, the 2nd of March, the President in the chair.

Mr. Arthur William Cooke, assistant to Mr. Fairley, was proposed as an Associate.

Mr. W. Chattaway was duly elected a member of the Society, and Mr. John Brown an Associate.

Dr. Vieth read the following paper :—

# ON THE COMPOSITION OF MILK AND MILK PRODUCTS.

By P. VIETH, Ph.D.

THE paper which I am about to read is the continuation of a series of annual reports which I have on former occasions submitted to the Society, and treats on the work done in the laboratory, which is under my charge, during the year 1891. (For former reports see THE ANALYST, vii., p. 53; viii., p. 33; ix., p. 56; x., p. 67; xi., p. 66; xii., p. 39; xiii., p. 46; xiv., p. 69; xv., p. 44; and xvi., p. 61).

The total number of samples analysed in 1891 is 21,885, viz. :

|                         |   |                        |
|-------------------------|---|------------------------|
| 19,849 samples of milk, |   |                        |
| 1,299                   | „ | cream,                 |
| 559                     | „ | skim milk,             |
| 40                      | „ | butter-milk,           |
| 119                     | „ | butter and butter-fat, |
| 8                       | „ | water,                 |
| 11                      | „ | sundry articles.       |

Of the milk samples 11,361 were taken from the railway churns in which the milk arrived from the country. Part of this milk is kept back for the production of cream; the bulk, however, is distributed with the least possible delay. Of the latter further samples—7,086 in all—were taken for analysis before, during, and after delivery for the sake of controlling the men who are entrusted with delivering the milk to the customers. The following table contains the monthly averages of the results of examination :—

AVERAGE COMPOSITION OF MILK.

| 1891.          | Samples taken  |           |      |              |                  |                  |                 |
|----------------|----------------|-----------|------|--------------|------------------|------------------|-----------------|
|                | On Arrival     |           |      |              | Before Delivery. | During Delivery. | After Delivery. |
|                | Spec. Gravity. | Tot. Sol. | Fat  | Sol. n. Fat. | Tot. Sol.        | Tot. Sol.        | Tot. Sol.       |
| January ..     | 1·0321         | 12·86     | 3·77 | 9·09         | 12·75            | 12·86            | 12·92           |
| February ...   | 1·0322         | 12·54     | 3·48 | 9·06         | 12·52            | 12·60            | 12·64           |
| March ...      | 1·0323         | 12·62     | 3·53 | 9·09         | 12·62            | 12·71            | 12·74           |
| April ...      | 1·0323         | 12·56     | 3·49 | 9·07         | 12·61            | 12·59            | 12·68           |
| May ...        | 1·0324         | 12·58     | 3·49 | 9·09         | 12·69            | 12·61            | 12·74           |
| June ...       | 1·0325         | 12·42     | 3·55 | 8·87         | 12·51            | 12·45            | 12·54           |
| July ...       | 1·0321         | 12·55     | 3·74 | 8·81         | 12·60            | 12·54            | 12·60           |
| August...      | 1·0320         | 12·70     | 3·90 | 8·80         | 12·71            | 12·72            | 12·71           |
| September ...  | 1·0322         | 12·93     | 4·05 | 8·88         | 12·87            | 12·89            | 12·90           |
| October ...    | 1·0323         | 13·17     | 4·22 | 8·95         | 13·12            | 13·08            | 13·17           |
| November ...   | 1·0321         | 13·21     | 4·30 | 8·91         | 13·06            | 12·99            | 13·10           |
| December ...   | 1·0321         | 13·02     | 4·15 | 8·87         | 12·88            | 12·83            | 12·95           |
| Yearly Average | 1·0322         | 12·76     | 3·80 | 8·96         | 12·75            | 12·74            | 12·81           |

The variations in the quality of the milk have been of the same character as in former years, that is to say, the richest milk was received during the last quarter of the year, and the poorest milk during spring and early summer. The year 1891 is, however, distinguished by the fact that the quality of the milk was for some months lower than in preceding years. The monthly average for June, and the yearly average for 1891, are the lowest monthly and yearly averages respectively, which I have observed since the commencement of my work here in 1880. The agreement between the results of the several series of analyses is satisfactory.

The solids not fat were found above 9 per cent. from January to May, but from June to the end of the year always below 9 per cent. This is a consequence of an alteration in the calculation of the fat, Fleischmann's formula having been used during the former, Hohner and Richmond's during the latter period.

The examination of 1,254 further samples of milk supplied on special terms gave results which were identical with those already mentioned.

Cream samples were taken for analysis before the cream was sent out, and while it was delivered to the customers. The total number of these samples was 999, and their average quality was as follows:—

AVERAGE PERCENTAGE OF FAT IN CREAM.

| 1891.              | Samples Taken    |                  |
|--------------------|------------------|------------------|
|                    | Before Delivery. | During Delivery. |
| January ... ..     | 46.6             | 47.0             |
| February ... ..    | 48.5             | 48.4             |
| March ... ..       | 49.8             | 50.2             |
| April ... ..       | 50.2             | 50.1             |
| May ... ..         | 49.8             | 50.0             |
| June ... ..        | 50.8             | 50.6             |
| July ... ..        | 50.4             | 50.3             |
| August ... ..      | 47.1             | 47.8             |
| September ... ..   | 50.1             | 50.1             |
| October ... ..     | 51.1             | 51.9             |
| November ... ..    | 45.7             | 46.3             |
| December ... ..    | 46.4             | 46.8             |
| Yearly Average ... | 49.0             | 49.1             |

The composition of 51 samples of clotted cream was as follows:—

|                |     |               |         |                 |
|----------------|-----|---------------|---------|-----------------|
| Total solids   | ... | 54.45 — 74.84 | average | 66.05 per cent. |
| Fat            | ... | 46.34 — 68.59 | „       | 59.30 „         |
| Ash            | ... | .12 — .77     | „       | .54 „           |
| Solids not fat | ... | 5.38 — 9.57   | „       | 6.75 „          |

The amount of fat left in skim milk, resulting when cream is abstracted from milk by means of centrifugal cream separators was, in the majority of cases, not higher than  $\cdot 3$ , and in a very few cases only above  $\cdot 4$  per cent.

The examination of 115 samples of butter gave the following results:—

*English Butter, fresh and salt.*—29 samples.

|              |     |     |               |         |       |           |
|--------------|-----|-----|---------------|---------|-------|-----------|
| Fat          | ... | ... | 81.59 — 90.92 | average | 86.88 | per cent. |
| Water        | ... | ... | 7.26 — 15.79  | „       | 11.08 | „         |
| Casein, etc. | ... | ... | .22 — 1.59    | „       | .59   | „         |
| Na Cl.       | ... | ... | .21 — 2.33    | „       | 1.45  | „         |

*French Butter, fresh.*—51 samples.

|              |     |     |               |         |       |           |
|--------------|-----|-----|---------------|---------|-------|-----------|
| Fat          | ... | ... | 82.77 — 85.39 | average | 84.64 | per cent. |
| Water        | ... | ... | 13.27 — 15.98 | „       | 13.93 | „         |
| Casein, etc. | ... | ... | .93 — 2.00    | „       | 1.33  | „         |
| Na Cl.       | ... | ... | .05 — .18     | „       | .10   | „         |

*French Butter, salt.*—5 samples.

|              |     |     |               |         |       |           |
|--------------|-----|-----|---------------|---------|-------|-----------|
| Fat          | ... | ... | 82.81 — 85.46 | average | 84.14 | per cent. |
| Water        | ... | ... | 11.13 — 12.98 | „       | 12.08 | „         |
| Casein, etc. | ... | ... | 1.65 — 1.97   | „       | 1.81  | „         |
| Na Cl.       | ... | ... | 1.62 — 2.26   | „       | 1.97  | „         |

*Danish Butter, salt.*—19 samples.

|              |     |     |               |         |       |           |
|--------------|-----|-----|---------------|---------|-------|-----------|
| Fat          | ... | ... | 81.37 — 86.52 | average | 83.80 | per cent. |
| Water        | ... | ... | 10.94 — 15.45 | „       | 13.35 | „         |
| Casein, etc. | ... | ... | .79 — 1.28    | „       | 1.02  | „         |
| Na Cl.       | ... | ... | 1.26 — 2.39   | „       | 1.83  | „         |

*Kiel Butter, salt.*—9 samples.

|              |     |     |               |         |       |           |
|--------------|-----|-----|---------------|---------|-------|-----------|
| Fat          | ... | ... | 78.83 — 87.78 | average | 85.01 | per cent. |
| Water        | ... | ... | 10.23 — 17.71 | „       | 12.33 | „         |
| Casein, etc. | ... | ... | .93 — 1.46    | „       | 1.13  | „         |
| Na Cl.       | ... | ... | 1.06 — 2.23   | „       | 1.53  | „         |

*Australian Butter, salt.*—2 samples.

|              |     |     |               |         |       |           |
|--------------|-----|-----|---------------|---------|-------|-----------|
| Fat          | ... | ... | 84.14 — 87.20 | average | 85.67 | per cent. |
| Water        | ... | ... | 10.72 — 12.22 | „       | 11.47 | „         |
| Casein, etc. | ... | ... | .85 — 1.33    | „       | 1.09  | „         |
| Na Cl.       | ... | ... | 1.23 — 2.31   | „       | 1.77  | „         |

In the case of French and Australian butter, the item “casein, etc.,” includes boracic acid in some form or other; in other butters I have not found preservatives.

The volatile acids—Wollny figures—found in the several classes of butter were as follows :—

|                |     |             |                   |
|----------------|-----|-------------|-------------------|
| English butter | ... | 24.0 — 29.3 | average 26.6 c.c. |
| French „       | ... | 26.0 — 30.0 | „ 28.1 „          |
| Danish „       | ... | 23.6 — 29.7 | „ 27.2 „          |
| Kiel „         | ... | 21.1 — 27.8 | „ 24.9 „          |
| Australian „   | ... | 30.5 — 32.5 | „ 31.5 „          |

The Wollny figures were below the normal—25 c.c.—in one sample of Danish butter, of the origin of which I know nothing; in five samples of English butter, the purity and genuineness of which I can guarantee, as the butters were churned, so to speak, under my eyes; and in four samples of Kiel butter. The last-mentioned samples\* came from the same dairy from which butter with abnormally low volatile acids had been received in 1889 and 1890, so that my experience with regard to this particular brand of butter extends now over three years. In every one of these years the Wollny figure was found to be below 25 from July to November, while during the remaining months it was normal. My friend, Dr. Schrodte, principal of the Dairy Experimental Station at Kiel, has investigated this case very closely, and his observations will soon be published in a paper which will appear in “*Die landwirtschaftlichen Versuchs-Stationen.*”

Dr. Vieth then read a paper on “The Average Composition of Milk,” after which Mr. Dyer read the following paper :—

#### FURTHER EXPERIENCE WITH ALKALI-GLYCEROL AS THE SAPONIFYING AGENT IN THE REICHERT PROCESS.

By H. LEFFMANN AND W. BEAM.

AN experience of about a year, during which several hundred determinations of oleomargarino have been made, with the alkali-glycerol as described in THE ANALYST (August, 1891), has convinced us that the method is accurate and expeditious. We wish to note here, briefly a modification which we have adopted. We find it of advantage to omit the previous evaporation of the water from the alkali-glycerol, thus securing a mixture which is sufficiently fluid to be measured without previous heating. The same volume of the mixture is used, and the evaporation of the water and saponification of the fat require but

\* The following are the individual results obtained at the times stated :—

1889.—25th June, 27.6; 2nd July, 25.9; 23rd July, 24.7; 6th August, 24.2; 15th October, 22.8; 5th November, 21.1; 4th December, 29.2; 10th December, 29.3.

1890.—30th July, 24.2; 14th October, 22.0; 28th October, 21.3; 18th November 26.1; 25th November, 26.2.

1891.—28th April, 27.6; 30th June, 25.3; 7th July, 25.6; 6th October, 21.4 and 21.1; 7th October 22.6; 25th November, 24.9.

a minute or two longer than when the previously concentrated liquid is used. It is also found to be more satisfactory in manipulation since the temperature does not rise so high during the saponification.

Mr. Leo Taylor then read a paper on "Reports on Water Analysis," and this terminated the Society's Proceedings.

### THE DRAWING UP OF CERTIFICATES.

By CHARLES E. CASSAL.

(Read at Meeting, February 3rd, 1892.)

It will be in the recollection of the Members of the Society that at a recent meeting of the Institute of Chemistry, a discussion took place on the "Ethics of Professional Certificates." Those who were present at that meeting will probably admit that the discussion was inadequate, no doubt in consequence of the intricacy, and especially of the tender nature, of the subject. I have no intention of dealing with it again here, much as it requires further discussion. My object in referring to the occasion is mainly to recall an observation of mine, which I desire to apply as a governing principle to the matter now in hand, namely, that the ethics of Professional Certificates cannot be held to differ fundamentally from the ethics of anything else; and that there is, or should be, nothing in professional chemical work whereby certain well-recognised principles of honour and of honesty should be disregarded, or to use a dangerous modern expression, "modified."

This being stated, it cannot be denied that from the professional point of view as well as from the standpoint of the general public, the method of drawing up Certificates and Reports, intended for official or public purposes or for private clients, is a matter urgently requiring our consideration, with a view of comparing our experiences, of stating our opinions, and if possible of arriving at some common basis of action, and of securing similarity of procedure at least to some extent.

The subject is necessarily one of much complexity, and I cannot hope to do more than introduce it in such a way as to serve as a "*point d'appui*" for a discussion. It would obviously be impossible to deal at length with the multiplicity of cases which occur in private practice, even if it were not an impertinence for any individual to attempt to do so; but the expressed opinions of the different members of the Society qualified to deal with the many and various branches of our work would, I think, if collated, enable us at least to see where we were.

Subject to the general principle of Ethics previously enunciated, I venture to put forward as my main contention that analytical data, and details of analytical processes should, as far as possible, be kept out of both reports and certificates. I am of course aware that in a great number of cases this procedure is not only impossible, but that the contrary is essential in regard at any rate to the giving of analytical figures. The

description of analytical processes in reports or in evidence is in my view to be absolutely condemned. But where figures are given, I hold that they should always be accompanied by an opinion or explanatory statement, and should be in the form of a separate report. It has been contended by some, that an analyst should confine himself in all cases to a bare statement of analytical figures, a view apparently arrived at in consequence of the unjustifiably absurd statements made—most frequently by persons who have no shadow of a right to practice analysis of any kind—upon altogether insufficient Analytical evidence, or upon no evidence at all. Such a contention cannot be maintained. To place in the hands of an ordinary client, or before a Public Board, a list of figures comprehensible only to experts, is an obvious absurdity. What is really wanted is the opinion of the expert, given clearly and definitely, and as far as possible in language that shall be “understood of the people.” What should be guarded against, and indeed, prevented as far as may be, are the erroneous conclusions and premature judgments of the non-expert or ignorant.

Dealing first with the certificates required from Public Analysts under the Acts, I contend most strongly that in *these*, analytical data should never, under any circumstances, be given. The contrary practice has been fraught with great evils to us as a profession, and has acted as a serious stumbling block to the efficient application of the Acts by the few Public Authorities possessed of sufficient collective enlightenment to try to apply them efficiently. Those who first introduced the statement of analytical data in official certificates no doubt acted in all good faith and according to their lights; but their proceedings were very unfortunate. Anyone who has been present in a Police Court and who has heard a magistrate, assisted by a solicitor or two, with the occasional intervention of an inspector and a defendant, struggling with “solids not fat,” “added water,” “fat and cream abstracted,” and so forth, must admit that analytical data are edge tools, wounding not only the ignorant—whose ignorance is generally of that dangerous character which leads them to believe they are wise—but also wounding those who have been indiscreet enough to bring these data forward in their certificates under the erroneous impression that, by so doing, they add to their reputation or magnify the value of their services. I am referring here to certificates relating to Milk, but my contention is universally applicable. Everybody concerned with them knows that the Adulteration Acts are cumbrous, and badly drawn, and that their provisions are apparently calculated to afford the largest possible number of opportunities for the escape of offenders. Still, under these Acts, it is not only quite unnecessary for a Public Analyst to give any analytical details in his certificates, but it is in contravention of the Acts to do so; a fact which makes the proceeding altogether indefensible, and indeed foolish. The 18th section of the Act of 1875 lays it down that the certificate of the analysis “shall be in the form set forth” in the schedule of the Act, “or to the like effect”—a very useful phrase. It is plain from this, that in order to meet the exigencies that might arise in the working of such Acts, discretion in the drawing of certificates is intended to be placed in the Public Analyst’s



hands. Moreover, the Act lays it down that the Analyst shall state in his certificate the *result* and not the *results* of his analysis, and while if the latter word were used in the Act, an ingenious lawyer, disregarding the spirit and intention of the Act, might endeavour to show that this meant analytical data; the word "result" clearly precludes any attempt of the kind from being successfully made before any fairly intelligent tribunal.

If the form of certificate contained in the schedule of the Act be adopted, a Public Analyst will use the formula, "I am of opinion that the said sample contained the parts as under," or "the percentages of foreign ingredients as under." In the case of extraneous water in milk the matter is simple enough. The Public Analyst is certifying strictly in accordance with the schedule of the Act when he reports that there is a particular quantity of extraneous water present; but the case is different when he has to deal with cases of abstraction. Cases of abstraction of any kind must necessarily be reported under the Acts as cases of adulteration, although the popular acceptance of the term 'adulteration' does not take account of such cases. It has been my practice to draw certificates, relating for example to the abstraction of fat from milk in this way:—"The said sample had had at least . . . per cent. of the original fat abstracted, and was therefore adulterated." It has been contended that this form of certificate is not in accordance with the schedule of the Act, as the "parts as under," or "percentages of foreign ingredients as under" have not been referred to. We are perfectly within our rights in using the words I have quoted. As I think I have shown, we are not compelled under the 18th section of the Act to use the terms of the schedule, and if it became necessary, it would be well to get our Authorities to fight the matter in the higher Courts. I believe that if that were done we should be perfectly successful. I have often been asked by those who have defended vendors, to give what the questioners were pleased to term "the parts." While for the reasons previously mentioned, I consider that such a demand need not legally be complied with, it may, nevertheless, be convenient to adhere to the form of the schedule until, at any rate, the question is fought out. The persons who ask for "the parts" in most cases really mean the analytical data, which, as I have said before, should never, under any circumstances, be given; and I unhesitatingly affirm that these are asked for because it has been found that by their production it is possible to throw enough doubt and confusion into a case to obscure the real issues, and thereby enable offenders to escape. I suggest a form of certificate to meet these cases, and I shall be glad to hear it discussed. A milk from which fat has been abstracted can be certified as containing "the parts as under"—namely so many parts of genuine milk, and so many parts of milk devoid of fat. It is a question whether the words "containing the lowest permissible proportion of fat" might not with advantage be inserted after the words "genuine milk" in the foregoing form, but I am myself disposed to think that this would only weaken the certificate. In the form suggested it will be found, of course, that the figure indicating the percentage of adulteration is the same as in the statement of "original fat abstracted." A certificate thus drawn clearly complies with the schedule of the Act; the statement made

in the certificate is strictly in accordance with scientific fact; it is, according to the analysis, the composition of the sample which has been submitted to the analyst, and the opposition are therefore bound to accept it.

With reference to Butter, if a Public Analyst stated in his certificate the analytical data upon which he based his opinion as to percentage of foreign fat, the ridiculous nature of the proceeding ought at once to be obvious to almost anyone. "Reichert figures," and "Koettstorfer numbers," "Insoluble and Soluble fatty acids,"—what are legal luminaries to make of these? A number of more or less ignorant people talk glibly enough in Courts of Law and elsewhere about the Total Solids, the Fat, and the Solids not Fat of milk, and this in consequence of what I cannot help characterising as the highly indiscreet action of several chemists; and although with reference to butter and to other foods this kind of thing is by no means so common, it is beginning to grow.

In this connection it will be remembered that, unfortunately, certificates issued by the Somerset House Chemists on samples of butter, state the percentage of fat, the percentage of water, and, if I remember rightly, of curd and of salt found in the samples. So far as I am aware there is no particular reason why this course should be followed. In reference cases these data have no bearing of importance on the points at issue, and even if they had I should contend that they should not appear in the certificates. Moreover, the fact that they do so appear, casts an entirely unjustifiable reflection on the Public Analyst, implying as it does that these data should also appear in the certificate issued by him. I am perfectly well aware that our friends at Somerset House have no desire to do anything of the kind, and it is to be earnestly hoped that they may be prevailed upon to discontinue the practice.

The Somerset House certificates on samples of butter afford a very apt illustration of my present argument. The percentages of fat, of water, and of curd, are given; these figures appeal to some extent to the ordinary mind and lead to the belief that a very "complete" analysis has been performed, and that the certificate is so much the more valuable and important. I hasten to say, in all sincerity, that I am sure that to no reason of this kind is to be attributed the action of the Somerset House Chemists; I point out the fact in order that the effect produced may be appreciated. When, however, we come to the other data that occur in butter analysis, we find that these are (very properly) not mentioned in the certificates. As we are all aware they go on to say something to the following effect,—“from a consideration of the results obtained on the analysis of the fat,” “we are of opinion that this butter contains such and such a percentage of foreign fat,” or “we are unable to affirm that the sample is adulterated.” It has no doubt been felt that to give the figures would be both injudicious and useless. Examples of the inadvisability and absurdity of giving analytical data in official certificates might be multiplied extensively. A striking instance is afforded by the Iodine-absorptions of lards and oils. But what applies to Iodine-absorptions, to Reichert and Koettstorfer figures, to Insoluble fatty acids and so forth, applies equally to “Total

Solids," to "Fat" to "Solids not Fat," and to "Ash." What has been done with disastrous results in the case of milk, what has been done with still more disastrous results in the case of water analysis, is being done in many directions and must produce equally bad effects.

Another point of importance in the drawing up of official certificates is the statement of percentages. I have heard it said that the statement of a minimum percentage is improper. Although, personally, I adopt the plan of stating a minimum percentage of adulteration in most cases, I fully admit that a good deal may be said in favour of a different course. From a practical police court point of view, it may be found better to adhere to a rigid statement of percentage. At the same time I may say that I have found, and I daresay my experience is not singular, that a good deal of wind is taken out of the sails of a cross-examiner by the use of the minimum statement. An opposite experience may have fallen to others. The matter is one which admits of much discussion, but I hold very strongly to the view that such a discussion should be carried out privately. We have foolishly provided and still provide our many enemies with quite enough information.

In reference to certain cases, such as, for instance, the use of preservatives—salicylic acid in beer, or boric acid in milk or butter, if a Public Analyst states a percentage of adulteration under these circumstances, he beforehand prevents the success of the case, and accusations are at once made against his Authority of having brought a "frivolous charge" against a "respectable tradesman." Taking the case of salicylic acid in beer, if the amount is stated in grains per gallon, it is a very different thing; it is understood and held then that a grave offence has been committed. In cases of adulteration with "preservatives," where an analyst may be called upon to state the amount of the adulterant, he can do so, in the case of such an article as beer, in grains per gallon; and in the case of such a substance as butter, in grains per pound. We have, as Public Analysts, to work under very defective Acts, and we have to deal with a comparatively ignorant public. Under these circumstances, we should be foolish indeed to allow ourselves to be taken advantage of, and not to adopt obvious precautions. Apart from the insertion of analytical details in certificates, it is a question whether quantitative statements of any kind can legally be demanded of us in a number of cases. In the Act of 1875 it is laid down, with certain reservations, that if an article purchased is not of the nature, substance, and quality demanded by the purchaser, an offence has been committed. The 2nd section of the Amendment Act of 1879, provides, that it shall be no defence to prove that the article in question, though defective in nature, or in substance, or in quality, was not defective in all three respects; that is, proceedings would be justified by defect in any one respect. Defect in *quality* is therefore a defect sufficient to justify proceedings under the Acts. The presence of an adulterant clearly constitutes defective quality, if nothing else. The adulterated article is not of the "quality" demanded by the purchaser. Defect in quality cannot necessitate the statement

of percentage. A percentage of quality cannot be stated, and under these circumstances such cases as are afforded by the use of so-called preservatives could, I contend, under the present law, be justifiably and sufficiently dealt with by a Public Analyst, by his certifying the article to be defective in quality, in consequence of the fact that it contained the preservative, without stating the quantity of the latter. The mere presence of "margarine", for example, is sufficient under the Margarine Act, irrespective of quantity, to constitute an offence under that Act. It ought not to be necessary, and I think I have shown that it is not necessary, to give figures in every case of adulteration, if the provisions of the Acts as they stand are adhered to; and hence, that a certificate drawn in accordance with this view, without giving percentages or parts of any kind, would in many instances be good in law.

The drawing-up of certificates in the great number of branches of analytical work and in the various cases that occur in general practice, is a very wide question, and for obvious reasons I do not propose to go into it at any length. Water analysis, of course, strikes one at first as a branch of analytical work, where the statement of figures in consequence of long custom has come to be almost essential. Probably no analyst of standing issues a report on a sample of water without stating his analytical figures; but while custom has made it almost necessary for this course to be followed, it is certain that, originally, it was not a wise one. Analytical details in water analysis whatever processes or combination of processes are adopted, are absolutely incomprehensible, to the majority of the people before whom they are placed.

Some persons adopting particular methods of water analysis, are in the habit of saying that all other methods are unreliable, and yield no results of value. This again affords an instance of the evil done by drawing up water analysis reports in the way in which they are generally drawn up at present. It affords opportunities for unprofessional squabbles, and allows of the real issues of a case being obscured. In the special case of water, I consider that the analytical report should invariably be accompanied by an explanatory report in which a full opinion is given, on the clear understanding that the analytical report is for the consideration of Experts; and that the opinion is for the direction of those who have consulted the analyst.

As an answer to the objection that it is essential to publish analytical details to justify the opinions that are given, I may bring forward the case of the Reports on the London Water Supply by the three analytical chemists who are employed on behalf of the London Water Companies. I will ask anyone who has studied these interesting documents, whether the analytical details given ever seem seriously to affect the equanimity of the analysts. The data in fact always enable them to take a roseate view of things, and that is a peculiarity of data, especially in Water Analysis.

There are cases where people want to know the percentage of a particular constituent, or the amounts of particular constituents. I have already admitted that there are a great

number of instances where the non-supply of analytical details would be impossible. There, of course, the matter does not admit of discussion. An analyst is employed for a particular purpose, and if what he is employed to do is professionally legitimate, he must do it; but I would say that very frequently in these cases the information is far more detailed than it need be, or, indeed, ought to be, considering the remuneration. Again, the publication of details of analyses may often be exceedingly useful to analysts who wish, for any particular reason, to cut up their professional brethren. While I say that, in the present condition of our profession, it may be necessary that nondescript hangers-on, and indeed, unfortunately, some members of it, should be dealt with severely in public, still this cannot be regarded as a desirable thing in a profession. The giving of analytical details may be useful for the purpose of exposing an incapable or ignorant man. It may be made useful also for showing those who are neither incapable nor ignorant how very absurd they may be made to look by quotations from their reports.

I say, finally, that it is most important for analysts to be agreed among themselves as to the course to be pursued. If one Public Analyst, for instance, has a prosecution undertaken on a certificate not showing data, and another Analyst, or worse still, another Public Analyst, appears in Court as a witness for the defendant and puts in a certificate showing quantitative details, the profession suffers. It is injurious to any profession that matters of this sort should be fought out in a police court, or indeed anywhere before an audience of the ignorant. Although I fear that I have hardly done justice to a subject which requires very full treatment and very careful handling, if the matter is adequately discussed by the members of the Society of Public Analysts, I have no doubt that useful conclusions will be arrived at. In this, as in all other matters affecting our profession, we must act together; united we can stand; divided, if we do not actually fall, it is certain that we shall never rise beyond the position we at present occupy.

#### DISCUSSION.

The President (Mr. Hehner) hoped that a considerable amount of discussion would take place upon Mr. Cassal's able paper. It touched upon a matter which affected every Public Analyst and every analytical chemist. He most heartily agreed with almost everything Mr. Cassal had said. It could not be expected that in a subject of such importance and magnitude they could all agree in every particular, but he had no doubt whatever that the observations of Mr. Cassal were worthy of their most careful consideration.

Analytical chemists were called upon to give two sharply-distinguished kinds of reports based upon analytical investigation. There were, first, the reports which were solely or almost solely wanted for the analytical figures given in them, such as percentage of gold or other metal in an ore, phosphoric acid in manure or manganese in iron. In these cases the clients on whose behalf the analyses were made, understood the exact significance of the figures. Then there was that large class of certificates, which included all certificates under the Sale of Food and Drugs Act, in which the analytical figures

were only the means of guiding the analyst to a correct conclusion, and in which, in the words of the Food Act, an opinion only was required. In these cases the figures were obtained, not for the client, but for the analyst himself. If an opinion on a sample of milk, butter or water was asked for, the analyst could not give that opinion without first making an analysis, and from this he formed his opinion. It could not matter to any client to what kinds of analytical processes the sample had been subjected, provided the analyst gave, to the best of his knowledge and ability, the opinion which was asked of him. Indeed, if figures were given in such cases, the analyst did something for which he had not been asked at all; and the figures in most cases would not only be entirely unintelligible to the client, but would actually confuse him. In other cases figures were positively dangerous, as they enabled unscrupulous persons to circumvent the efforts of the Public Analyst, as in the case of milk and butter. He regretted very much that there had ever been any public mention of such terms as solids not fat, insoluble fatty acids, Reichert figures, and such like. These were scientific matters which they should discuss between themselves and for professional advancement; yet by the mistaken anxiety of analysts to justify their reports, they had become terms with which the public was now familiar. In time the analyst might be expected to go still further and to tell his clients every step he took to get at a result. Although he had for a long time refused to give his clients any information as to the processes of analysis adopted, which would be done in the case of articles of food if analytical figures are given, yet he had from time to time been positively requested to furnish analytical figures. He had made it a rule, rather to refuse and return the samples than to give this information, unless very strong reasons were given for so doing; because he could perceive that the figures in many cases like this were wanted for the purpose of defeating the efforts of Public Analysts. As soon, for instance, as it was known, what percentage of fatty acids or what Reichert figure would pass a sample of butter as genuine, certain dealers at once worked up or down to these limits.

On the other hand, it would have to be acknowledged that it would be impossible, without analytical figures, to judge what value attached to any particular certificate, for figures in many cases could be checked, proved or disproved. But even figures were not always conclusive evidence of *bond fide* work. He believed that any dishonest proceeding in analytical practice must defeat itself in the end. The value of the certificate could not be measured as a rule by the figures which might be contained in it, but rather by the signature at its foot. Then there was another question, which he believed had much to do with the giving of figures in reports; where such had not been asked for analysts had an impression that they must show something for their fees. An opinion occupying, perhaps, two lines of a certificate, might possibly not appear to a client, who may not know, that these few lines may be the outcome of a lengthy analysis or investigation, and of a great deal of laborious work, to be worth two, three or more guineas; whilst a formidable array of figures would constitute a claim for a respectable bill. This view of the case

was confirmed in his mind by the Continental practice of charging for every single determination, or even for every single weighing, the price lists of Continental analysts setting often forth the ridiculously small sums charged for each item, and which, like lawyers' bills, might yet amount to a considerable total. He thought that this was a very degrading way to look upon an analysis and the duties which one owed to one's client. It tended to make the analyst a mere analysing machine who made certain determinations at the bidding of his client.

As to figures in water analysis, nothing was more common than to receive a request from an otherwise intelligent client, to test any particular sample for purity, with the intimation that an analysis is not required; thus clearly showing that the client often thinks the analytical figures so constantly given in water analysis are to him an unnecessary piece of information. And, as a matter of fact, it appears to me nothing short of absurd, to furnish the public, in reply to a request for an opinion as to the purity by the water supply, with a long string of figures, which has not been asked for and which is unintelligible to by far the majority of educated men. It is only the Analyst's Report, that is to say, his opinion, which is wanted, and not his figures at all. These were unmitigated evils, and he hoped that the practice would be dropped.

It had been stated by Mr. Cassal that he thought the word "quality" mentioned in the Act might be used in connection with the suppression of preservatives in butter, and that it might be said that the article was deteriorated in quality by the addition of preservative. He (the President) thought that the word "quality" as used in the Act must be construed in the common sense and not in the analytical sense; and he could not think that a substance which was added to butter with the intention, and with the effect, of preserving the butter as to quality, could be condemned as if the quality of the article were thereby deteriorated.

Mr. G. Embrey considered that Mr. Cassal's paper raised one of the most important questions which they could discuss, and that, whilst agreeing generally with Mr. Cassal's opinion as regards certificates of food, he could not entirely agree with him in his views with respect to certificates relating to water. In regard to food, he might mention that some years ago he was in the habit of giving the total solids and fats, until some magistrates who were much wiser than he, thought it only gave solicitors an opportunity of making a muddle of their cases, and the climax was reached when a solicitor, who had been reading a book on Food Analysis, asked him if he had estimated the amount of lactochrome in a milk analysis. He then gave up the practice; and since that time he had never given figures. He had had a case in which a solicitor had objected that he (Mr. Embrey) had not complied with the Act of Parliament, but the case was dismissed for another reason. Coming to the question of water analysis, he disagreed with Mr. Cassal altogether; there were so many humbugs, and it was so difficult to detect them. There were Medical Officers of Health, who analysed samples of water for absurdly low

fees. There were plenty of Medical Officers of Health—there were several in his own county—who, when they received a sample of water, put it into a wine-glass, added some pyrogallie acid, and then some salt, allowed it to stand, and if it turned black condemned it as unfit to drink. These people, in their reports, simply stated that the water was unfit to drink; they gave no reason for their statement, they could not give figures, because they were incapable of performing an analysis. He believed that if, in the case of water analyses, one did not give figures, one would not get paid.

Mr. Cribb said that he had seen in a trade journal a report of a police court case, in which an analyst certified that a sample of butter contained no less than 99 per cent. of fat "other than that of butter." He was always under the impression that it was impossible for butter or margarine to contain 99 per cent. of fat of any kind. As regards the method of drawing up certificates for butter adulteration, he was aware that many analysts calculated the percentage of foreign fat upon the fat itself, and then assumed that that percentage held good for the whole butter. But was there any justification for this assumption? If, on the other hand, the water, salt, and curd were determined and considered as belonging to the *butter* and not to the adulterant, and allowance made accordingly, then it appeared to him that the actual percentage of adulteration was being considerably under-stated. At the same time he thought it was the only correct method if the sample was certified, as containing a percentage of *foreign fat*, as obviously water, salt, and curd (though partly belonging to the adulterant) could not be included under this head. He should be glad to hear the opinions of others on this point. With respect to cheap analysis of water, he would like to mention, as an illustration of the unprofessional conduct which is rife at the present time, that having as clients of some years standing, a firm who sent him a large number of waters, another analyst had made them an offer to do the same analyses for half the usual fee; and, having been refused, actually offered to do the work for nothing in the hope of gaining a certain amount of publicity in the brewing trades with which the firm were connected. Regarding the question as a whole, he entirely agreed with Mr. Cassal, that figures should not be given in analytical certificates, except in certain cases. He would hesitate to adopt Mr. Cassal's suggestion as to skimmed milk certificates, on account of the difficulty of making the matter clear to the magistrate. He spoke feelingly on the subject, for the reason that recently he had had to attempt to explain to an ordinary lawyer, how the percentage of added water was calculated from the results of a milk analysis; and after an expenditure of not less than 30 minutes, the solicitor left and went away, saying that he thought there must be some fallacy in the method of calculation.

The President said that if a sample of butter were brought to an analyst, he was asked whether it consisted of genuine butter or whether it were mixed with margarine, and in that case with how much margarine? It seemed to him that it was taking up a mistaken position if the analyst, in his Report, made any reference whatever about "fat" or any other constituent of butter, as he was asked nothing about these,



The Act of Parliament required a statement of the percentage of foreign ingredients, but the foreign ingredient in a sample of adulterated butter was margarine, not foreign fat. Butter and margarine in themselves consisted of water, curd, salt, and fat, therefore the article, as a whole, had to be considered and reported upon, and not any particular constituent of it.

As regards the statement of results, and the question whether any calculation was required to deduce from the analysis of the fat the percentage of margarine or butter, he would point out that, as both butter and margarine contained each about 15 per cent. of matters other than fat, the proportion of mixture in the fats melted out from the whole was still the same as in the original article. Therefore, if on analysing the fat itself, it were found that it was a mixture of 80 parts of butter-fat and 20 parts of other fat, then the original article had also been mixed in these proportions.

As a further instance of the mischief made by analysts in giving analytical figures for which they were not asked, he might say that he (the President) had formerly always been in the habit of stating the strength of samples of spirits taken under the Food Acts in percentages under proof, adding, in the case of dilution, the percentage of added water. As the latter was deduced by calculation from the former, but was of course not identical with it, explanations had from time to time to be given to enquiring magistrates, with unsatisfactory results, until he was at last requested in future to give no figures in spirits whatever, except on the percentages of added water. There could be no doubt that that was all the magistrate wanted. All certificates that had to go before a court of law ought to be as simple and as unencumbered with unnecessary matter as possible, such information being entirely reserved for oral evidence, if necessary.

Mr. Sidney Harvey said that soon after he joined the Society he asked the late Mr. Wigner whether the time had not come to have a fixed mode of drawing up their official reports. He felt very much at sea upon the subject, as he had only just commenced work as a Public Analyst. He was told by that gentleman, and by others, that it was not wise to coerce Public Analysts in the matter, but that it was best to allow them to adopt their own methods. He (Mr. Harvey) regarded that as a great mistake, and he had waited to see if some one would "bell the cat." He now found that he had been a great sinner in this procedure, for, in the absence of anything like precedent, he *had* furnished figures, and very much for the reason that unless one gave figures, public bodies thought one did not earn one's money. At the same time, figures had got him into a great deal of trouble and he would, in future, refuse to give them. All, it appears, he had to do was to state the probable proportion of the adulterating ingredient. With regard to waters, his experience had been a singular one. When he first made official statements as to purity of waters and their fitness for drinking purposes, several authorities begged him not to give figures at all, but simply to say whether the water was fit for drinking purposes or not. But when it became a rule in his part of the country, that reports were sent straight to the Medical Officer of Health, by whom they were endorsed, the case wa

somewhat altered. He made a statement of the purity of the water on one page, and he gave a list of figures upon which he founded his opinion on the other. It appeared to him that in such a complicated matter as a water analysis, it was very desirable that as many data as possible should be accumulated in every case; although he must admit that local authorities often blundered over the figures, and thus caused a very great deal of trouble. He had been reminded, for instance, of the fact that fifteen or sixteen years ago, he had passed waters containing large amounts of nitrates which he had since ceased to do. He apprehended that the remarks made by previous speakers did not apply to manures, &c., but were entirely confined to the work of Health Analysts, and Public Analysts.

Mr. Robert H. Davies remarked that Mr. Cassal had indicated certain cases in which it was desirable to express results in other ways rather than in percentages; this had long been the practice in stating the amount of alum in bread, in which the number of grains per 4lb. loaf were given. He generally agreed with the observations made by the reader of the paper, and also acknowledged the wisdom of omitting analytical results wherever possible, from official certificates. He himself had been in the habit of giving figures, simply because the chemist, with whose methods he was best acquainted when he commenced practice, was accustomed to do so. As regards the wider question, whether ordinary certificates and reports should include analytical figures, that appeared to him to present great difficulties. In many cases clients, who understood the meaning of the figures, would much like to have them, and would not be satisfied with a bald statement to the effect that, say, a sample of milk or butter was pure or impure. He could not see how, in such cases, the analytical figures could be refused.

Mr. Cassal, in reply, said he was glad that a discussion of some value had taken place. He hoped, however, that the matter would be discussed again before long. It was a subject upon which so many men were competent to speak, and ought to speak, that it would be a great pity, if, in the near future, a discussion could not be again arranged, so that the profession could have the benefit of additional opinions. He noted, with much satisfaction, the general agreement of the members present, that the old practice of stating analytical details in certificates given under the Acts, was irregular and objectionable; that it was injurious to the profession, of no value to magistrates, or to the public, and that it ought to be entirely given up by all Public Analysts. In this connection Mr. Davies had given an example of the evils of precedent, by citing the case of the district where, in the remote past, the analyst had been in the habit of giving, in certificates on samples of butter, the percentages of water, of fat and of curd, and where, in consequence, this mistaken practice had been continued to the present day.

The President had truly said that an analysis was, in reality, the private property of the analyst. Those cases where the amounts of particular constituents were required, were of course to be excepted. He (Mr. Cassal) specially excepted those cases, although he would again point out that in many instances far too much information was given,

even for private clients ; and this for the bad reason, that it tended to produce in the minds of clients the notion that the analyst who followed this course was superior to other analysts. In fact, it was done with the idea that more "business" would thereby be obtained. This was a mistake. He did not believe that professional work was increased by this kind of procedure. If he was wrong, and the opposite was the case, then he contended that such a method of increasing work was professionally illegitimate.

The argument that the giving of figures would prevent the practice of analysis by unqualified and incompetent persons nevertheless required careful consideration. This was to be distinguished from the case of one qualified and competent man trying, by the giving of figures, to get the better of another. Mr. Embrey had given the meeting some startling instances. He (Mr. Cassal) had never yet heard of medical men "performing analyses"—and what performances they must be—for the trumpery fees mentioned by Mr. Embrey. It was unfortunately true that certain medical men were in the habit of giving puffing testimonials founded upon no analytical evidence whatever ; while others, devoid of special training and engaged chiefly in medical work, very improperly undertook the analysis of water and foods.

Would the giving of analytical details by professional analysts put a stop to this kind of thing ? He thought not. As a preventative it was insufficient. The generality of people were not sufficiently intelligent to grasp the difference between a report which contained figures, and a report which did not, and to distinguish by that means between the man who had a right to report and the man who had no such right. Other and more powerful means should be adopted. The Society of Public Analysts existed not only for the discussion of scientific matters of interest to its members, and of public importance but it existed also for the discussion of matters that were of vital professional importance ; and it was of vital importance that such a state of things as that described by Mr. Embrey should not be tolerated. The Society could, if it chose, take up a strong position in the matter, and the members, by united and resolute action, could largely prevent the unfair and degrading competition that had been described. The time was rapidly approaching when what he might call "Professional Unionism" would be a necessity, and he did not see why it should not now be openly and boldly advocated.

In reply to Mr. Harvey, he desired to say that he did not intend to limit the suggestions made in the paper to official analyses under the Acts and to matters relating to Hygiene. There were many other cases where it was injudicious to give figures. The analysis of oils afforded an example. A Public Board, buying a number of different kinds of oil, would submit samples of these for analysis. It would be injudicious to put analytical details into the Report, which, of course, was a Report issued by an analyst acting in his private capacity. The analyst would be acting wrongly and foolishly if he gave the data upon which he based his opinion that a sample of colza oil was adulterated with mineral oil. He had admitted that he was somewhat uncertain as to what could be

done at present in reference to water. In introducing the discussion, he had said that it would be a matter of very great difficulty at the present time to refuse to give analytical details in reporting on waters. In certain other special cases, and to *bond-fide* private clients, it might be necessary or advisable to give analytical figures, when it was known that such figures would probably not be made use of in any way that might be detrimental to the profession. After all, in most cases, it was the analyst's opinion that was required. If people had confidence in him they took his opinion; if they had not that confidence they did not.

In conclusion, Mr. Cassal urged that in all matters of dispute the Council of the Society of Public Analysts should be appealed to, as representing the only scientific and professional body in the Country having the right to give authoritative opinions on analytical matters and he again insisted on the necessity of united action.

**Rum and its Adulteration. A. Scala.** (*Gazzetta. Chimica. Italiana.* 1891—396.)—After a lengthy discussion of the origin and adulteration of rum, the author gives the composition of 5 rum essences, used at Rome for adulteration.

|   | Formic ether | Acetic ether | Alcohol vol. | Alcohol vol. | Extract | Ash  | Colour  | Smell    |
|---|--------------|--------------|--------------|--------------|---------|------|---------|----------|
| 1 | 0.46         | 9.11         | 68.76        | 61.13        | 1.98    | 5.02 | Caramel | Cinnamon |
| 2 | 0.95         | 6.11         | 78.40        | 63.45        | 3.18    | 0.06 | "       | "        |
| 3 | 0.77         | 8.93         | 59.34        | 51.50        | 2.53    | 0.04 | "       | "        |
| 4 | 0.76         | 13.02        | 49.91        | 42.33        | 7.94    | 0.15 | "       | "        |
| 5 | 1.36         | 26.90        | 44.50        | —            | —       | —    | "       | "        |

$\frac{\text{Formic ether}}{\text{Acetic ether}}$  1 : 6.43 to 1 : 19.8.

All 5 samples gave a strong Schiff's reaction.

The total ethers were estimated by saponification, and the Formic ether by the quantity of reduced mercurous chloride obtained on warming the neutralized saponified solution with mercuric chloride; the difference between the alkali required to saponify the total ethers and that for the Formic ether was calculated to Acetic ether, though other ethers (Butyric) were proved to exist.

The substantial accuracy of these methods was proved by experiment.

The author also analysed a genuine Martinique Rum, an artificial one, and 7 samples bought in Rome.

|   | Name       | Price per litre | Formic ether | Acetic ether | Alcohol |        | Extract | Ash  | Amyl alcohol | Schiff's test | Reaction with sulphuric acid |
|---|------------|-----------------|--------------|--------------|---------|--------|---------|------|--------------|---------------|------------------------------|
|   |            |                 |              |              | Volume  | Weight |         |      |              |               |                              |
| 1 | Martinique | —               | .012         | .297         | 52.01   | 44.36  | .364    | .062 | .266         | V. weak       | Strong                       |
| 2 | Artificial | —               | .028         | .180         | 55.83   | 48.05  | —       | —    | .169         | Distinct      | Weak                         |
| 3 | Jamaica    | 7 litre         | .004         | .140         | 60.85   | 53.00  | .554    | .018 | .066         | "             | None                         |
| 4 | —          | 2.5 "           | .006         | .032         | 43.13   | 36.17  | .194    | .016 | .047         | None          | "                            |
| 5 | —          | 3 "             | .006         | .089         | 34.67   | 28.69  | 2.047   | .011 | .073         | Distinct      | V. weak                      |
| 6 | —          | 4 "             | .001         | .141         | 47.89   | 40.50  | .810    | .028 | .208         | "             | Strong                       |
| 7 | —          | 3 "             | .005         | .071         | 47.02   | 39.70  | .996    | .012 | .150         | None          | V. weak                      |
| 8 | —          | 2.5 "           | —            | .024         | 38.89   | 32.37  | 2.212   | .012 | .033         | Weak          | None                         |
| 9 | —          | 4 "             | .009         | .056         | 52.91   | 45.23  | .654    | .020 | .192         | "             | Strong                       |

The characters of the aqueous distillate were :—

- |  |                                     |
|--|-------------------------------------|
| 1.—Gave a very strong persistent smell of Rum. | 6.—Gave fairly strong        "      |
| 2.—"    a foreign odour.                       | 7.—"    very weak         "         |
| 3.—"    no odour of Rum.                       | 8.—"    no smell.                   |
| 4.—"    very weak odour of Rum.                | 9.—"    fairly strong odour of Rum. |
| 5.—"       "       "                           |                                     |

He concludes that natural Rums can be distinguished from artificial or watered Rums by:

1. The quantity of ethers, alcohol [? amyl. Abs.], which is different in artificial and watered Rum to that in natural Rum.

2. The reaction of sulphuric acid on the aqueous distillate [the portion left in the retort], giving a rose-violet with natural Rums, and less intense or absent in adulterated or artificial Rums.

3. The smell of the aqueous distillate when rubbed on the hand is very strong and persistent with natural Rums, and less so or absent with diluted or artificial Rums.

H. D. R.

[NOTE BY ABTRACTOR.—The author had overlooked the fact that distillation with a very perfect dephlegmator gives a rum containing much less of the impurities on which his methods of distinction depend; it is unlikely that No. 3 in his list, for which was paid the highest price of all, should be entirely artificial, as he is inclined to conclude.]

**The Examination of Platinic Chloride for Purity.** A. F. Holleman. (*Chem. Zeit.* 1892, xvi. 35).—The usual tests for the purity of platinic chloride, namely, that it should dissolve clear in absolute alcohol, and the residue left by its ignition should yield no soluble matter when treated with dilute nitric acid, do not give sufficient information. A sample answering to these tests gave unsatisfactory results in the determination of potassium, and upon examination proved to contain sulphuric acid in appreciable quantities. It is, of course, absolutely necessary that this acid should be absent, both for the reason which leads to the scrupulous removal of all sulphates previous to the precipitation of potassium platinic chloride, and also on account of the likelihood of a trace of barium chloride (used for removing sulphates) being present in the solution of the alkali to be precipitated, which would, if neglected, cause the precipitate of potassium platinic chloride to be contaminated with barium sulphate, should the platinic chloride contain sulphates.

B. B.

Mr. H. Droop Richmond, late of the Khedival Laboratory, Cairo, has been appointed Chemist to the Aylesbury Dairy Company, *vice* Dr. Vieth, *resigned*.

# THE ANALYST.

MAY, 1892.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A meeting of the Society was held on Wednesday, the 6th of April, the President being in the chair.

The minutes of the last meeting were read and confirmed.

The following gentlemen were proposed as members :—Mr. Percy Gerald Sanford, F.I.C., F.C.S., Analytical Chemist, 20, Cullum Street, Fenchurch Street, E.C.; Mr. Harry Silvester, F.I.C., F.C.S., Analytical Chemist, Holyhead Road, Handsworth, Birmingham; Mr. L. J. de Whalley, B.Sc. (London), Chemist in charge at Messrs. A. Lyle and Sons, Limited, Plaistow Wharf, Victoria Docks, E.; 26, Park Place, Greenwich, S.E.

Mr. J. Shorthouse Tweedie was proposed by the Council as an Associate.

Mr. Arthur William Cooke, F.C.S., Analytical Chemist, Portland Cottage, Ings Road, Wakefield, was duly elected as a Member of the Society.

Mr. C. E. Cassal read a paper "On a recent Case of Butter Adulteration." A discussion followed, after which Mr. Dyer read the following paper:—

## ON THE INAPPLICABILITY OF THE WERNER-SCHMID METHOD OF THE ANALYSIS OF CONDENSED MILKS.

By BERNARD DYER, B.Sc., and E. H. ROBERTS.

BOILING cane-sugar with hydrochloric acid results in the production of caramelised matter which is soluble in ether.

Quantities of cane-sugar, varying from 0.6 to 0.8 gramme, were dissolved in each case in 10 c.c. of water, the solution being boiled with HCl, and treated in the Werner-Schmid tube exactly as in a milk analysis. Ether residues were obtained, varying from 0.018 to 0.024 gramme, equal to from 0.18 to 0.24 per cent., comparing the fluid with milk.

Milk sugar gives no such residue, not more than 0.002 gramme being obtained in six experiments like the foregoing, milk sugar being substituted for cane sugar.

Experiments with milk to which cane sugar had been added, in proportions varying from 5 to 10 per cent., gave apparent percentages of fat by the Werner-Schmid method, ranging from 0.12 to 0.32 per cent. higher than the actual percentages obtained by the Adams process. Taking into account the necessary dilution of condensed milk, such errors would be multiplied up to from 0.6 to 1.6 per cent.

The authors conclude that the Werner-Schmid method, which gives quite accurate results for unsweetened milk, is inapplicable for sweetened condensed milk.

They also find that the Adams process, the milk being sufficiently diluted, and 5 c.c. only of the solution being used, is satisfactory for determining the fat even in highly-skimmed condensed milk.

#### DISCUSSION.

Mr. A. W. Stokes said that he also had, from recent experiments, noticed that some caramel was extracted with the fat in the Werner-Schmid process as ordinarily conducted. Dry caramel Mr. Stokes believed to be practically insoluble in ether, but as ether takes up some water, partly in solution and partly mechanically suspended, and as caramel is freely soluble in water, it naturally follows that in the Schmid process some caramel is extracted with the fat in the case of a condensed milk. If, however, after drying and weighing this extract in a flask or beaker, this be washed out several times with ether, it will be found that the ether takes up no caramel. In re-weighing the flask and subtracting its present weight from the former, the true weight of the fat will be obtained.

The advantages of the Schmid process for condensed milk are that a comparatively large quantity of the milk can be taken for analysis, and errors due to high multiplication for percentages are avoided.

In Mr. Stokes' experience the paper-coil method, owing to the presence of so much sugar, does not give the whole of the fat actually present in a condensed milk. Figures of analysis bearing out these contentions were adduced.

Mr. H. Droop Richmond protested against Mr. Stokes putting down certain figures on the board and calling them fat estimated by the Adams process, when, as a matter of fact, the process used was a modification. The advantage of the Adams process over others was, that the finely-divided fibres of the paper caused separation between the watery parts of the milk and the other part; and if a greater quantity of milk was placed on the paper than could be absorbed this condition was not attained. It was an essential point in Adams' method that a quantity, not greater than could be all absorbed, should be put on the coil, otherwise no separation took place, and it was better than direct separation to use 10 c.c. to one coil. He was sorry that this point had not been more strongly insisted upon. Separation would not take place with the method as used by Mr. Stokes

and this accounted for his low results. He might say that he had made some experiments with condensed milk. He had extracted the fat both by the Adams' process and by precipitating the casein, and the results had been almost exactly alike, with a slight advantage to the Adams process.

Mr. Bernard Dyer said that his experience quite agreed with Mr. Richmond's. If 5 c.c. of fluid were distributed over a strip of paper of a certain size, it was a different thing from distributing over a like surface 10 c.c. of a more dilute fluid. If 10 c.c. of milk were placed on an ordinary "Adams" strip of paper it was made almost "sloppy"; but if 5 c.c. were put on, slowly and gradually, that quantity barely seemed to wet the whole paper. The "selective" action of the paper came into play, and caused a separation of the fat, which could be traced as the paper dried. Even highly-skimmed condensed milk could be accurately analysed in this way. But if 10 c.c. of the diluted milk were taken, the conditions were altogether altered, and the result was the production of a film of "toffee" which the ether could not permeate.

#### A RAPID AND ACCURATE METHOD OF DETERMINING FAT IN MILK.

BY HENRY LEFFMANN, M.D., AND WILLIAM BEAM, M.D.

AMONG the processes for the rapid determination of fat in milk, those employing centrifugal machines have been most satisfactory. A procedure devised by us has proved, in the experience of others as well as of ourselves, to be rapid, accurate, and economical. For the test, we employ a bottle holding about 30 c.c., the neck of which is graduated, so that a volume of  $1\frac{1}{2}$  c.c. is divided into 86 equal parts. 15 c.c. of the milk being taken, each of these represents 0.1 per cent., by weight, of butter-fat. The test is made as follows:—

15 c.c. of the milk are put into the bottle, 3 c.c. of a mixture consisting of equal parts of fusel oil and strong hydrochloric acid are added, mixed, and strong sulphuric acid poured in slowly, with agitation, until the bottle is filled nearly to the neck. The liquid becomes hot, and the casein is completely dissolved, a dark reddish-brown solution being formed. The neck is filled to near the zero point with a hot mixture of sulphuric acid and water, and the bottle whirled in the centrifugal machine for from one to two minutes. Milk very poor in fat may require from three to four minutes. The volume of fat which rises in the neck can be read off directly, or by the use of a pair of dividers. The points of these are adjusted at the upper and lower limits of the column of fat, allowance being made for the meniscus, then, the dividers being placed so that one point coincides with the zero of the scale, the exact volume can be read off. If but one test is to be made, it will be necessary, of course, in order to preserve the balance of the arms of the machine, either to make duplicate mixtures, or to fill the other test-bottles with diluted sulphuric acid.

We give herewith the results of comparative tests with the Adams' method, care being taken that the paper used was free from any extractable matter. The bottles



employed in these tests were divided into 100 parts, and the figures here given were obtained by multiplying by the factor 0·86. (As noted above, we now use a bottle divided into 86 parts, and thus save calculation.) :—

| WHOLE MILK.               |                       |     |       |     |                            |   |
|---------------------------|-----------------------|-----|-------|-----|----------------------------|---|
| Sample.                   | Fat by Adams' method. |     |       |     | Fat by centrifugal method. |   |
| No. 1                     | ...                   | ... | 3·534 | ... | ...                        | $\left\{ \begin{array}{l} 3\cdot53 \\ 3\cdot56 \\ 3\cdot56 \end{array} \right.$ |
| No. 2                     | ...                   | ... | 3·90  | ... | ...                        | $\left\{ \begin{array}{l} 3\cdot95 \\ 3\cdot99 \\ 3\cdot95 \end{array} \right.$ |
| No. 3                     | ...                   | ... | 3·03  | ... | ...                        | $\left\{ \begin{array}{l} 2\cdot97 \\ 2\cdot97 \\ 2\cdot93 \end{array} \right.$ |
| SKIMMED AND WATERED MILK. |                       |     |       |     |                            |   |
| No. 4                     | ...                   | ... | 0·56  |     |                            | $\left\{ \begin{array}{l} 0\cdot51 \\ 0\cdot51 \end{array} \right.$             |

Another determination was made of sample No. 4 by boiling down to one-half volume, and treating by the method, the results being calculated to the original volume. This gave 0·55 per cent. of fat.

Tests were made to determine the effect of longer rotation in the examination of milks poor in fat. Thus, by four minutes' whirling, the last sample gave, without previous concentration, 0·55 of fat.

Comparisons have also been made between the results of this method and the figures for fat as determined by calculation from the specific gravity and total solids (Hegner and Richmond's tables).

| Sample. | Fat by calculation H. and R. |     |      |     | Fat by centrifugal method. |      |
|---------|------------------------------|-----|------|-----|----------------------------|------|
| No. 5   | ..                           | ... | 3·60 | ... | ...                        | 3·61 |
| No. 6   | ...                          | ... | 4·15 | ... | ...                        | 4·10 |

We find, as a result of many tests, that with bottles accurately graduated, and reasonable care in manipulation, especially sufficient rotation, results will be obtained within 0·1 per cent. of those of the standard methods.

715, Walnut Street, Philadelphia, U.S.A.

This terminated the Proceedings of the Society.

## THE AVERAGE COMPOSITION OF MILK.

By P. VIETH, PH.D.

*Read at Meeting, April, 1892.*

By the kindness and indulgence which the members of this Society have extended to me in such a great measure during the last ten years, I have been permitted from time to time to lay before the Society annual reports on the work carried on in the laboratory of

which I have been in charge since the year 1880. The most prominent, and perhaps also the most important figures--certainly the figures based upon the largest number of analyses--were those showing in monthly averages the composition of samples of milk as received from the places of production, *i.e.*, the farms situated in different parts of the country on which the cows were kept. The aim constantly kept in view was to examine as many samples as circumstances would permit, and, indeed, it has been the practice to ascertain the specific gravity of the contents of every single churn of milk arriving from the country, a test which, in the greatest majority of cases, would at once draw attention to any abnormality in the quality of the milk. The specific gravity was always corrected to 15°C. As to the analysis of the milk samples this had to be limited to the usual items, *viz.*, total solids, fat, and solids not fat. There has never a change been made with regard to the determination of total solids, for which 5 grms. of milk are taken and dried in a platinum capsule, first three hours on the steam bath and then three hours in the air bath at from 95 to 100°C. Fat was determined by means of the lacto-butyrometer up to July, 1884; since August, 1884 it has been calculated from specific gravity and total solids. Up to April, 1885, the formula used was that constructed by Fleischmann and Morgen; from May, 1885, to May, 1891, Fleischmann's corrected formula was employed; and since June, 1891, the formula of Hefner and Richmond. It is obvious, then, that results referring to fat--and also to solids not fat which were always taken by difference,--obtained at the various periods mentioned are not directly comparable. As I do not expect that another alteration in the manner in which the work is carried out will take place, or even if it should take place, that the results would be materially affected, I thought it desirable to re-calculate all the earlier results from the formula of Hefner and Richmond, and represent the corrected and strictly comparable results thus obtained in a diagrammatic form which shows the prominent points clearer than long columns of figures.

From the diagram it will be seen that the monthly averages varied between the following limits:--

|                |     |     |     |                       |
|----------------|-----|-----|-----|-----------------------|
| Total Solids   | ... | ... | ... | 12.4 to 13.6 per cent |
| Fat            | ... | ... | ... | 3.6 „ 4.6 „ „         |
| Solids not fat | ... | ... | ... | 8.6 „ 9.1 „ „         |

The average composition of the 120,540 samples examined during the last eleven years is--

|                |     |     |     |                |
|----------------|-----|-----|-----|----------------|
| Total Solids   | ... | ... | ... | 12.9 per cent. |
| Fat            | ... | ... | ... | 4.1 „ „        |
| Solids not Fat | ... | ... | ... | 8.8 „ „        |

A single glance at the diagram reveals the well-known fact that the variations in the amount of total solids are mainly due to variations in the amount of fat. I say deliberately "mainly" and not "exclusively," for looking more closely into the figures, we find that a larger percentage of total solids is, generally speaking, accompanied, not only by a rise in fat, but also, although to a very much smaller extent, by a rise in solids not fat.

The following figures will make this clear:—

|  |   |   |   |      |   |
|--|---|---|---|------|---|
| 12·5 total solids are accompanied on average by 8·70 solids not fat. |   |   |   |      |   |
| 12·6   | " | " | " | 8·83 | " |
| 12·7   | " | " | " | 8·80 | " |
| 12·8   | " | " | " | 8·83 | " |
| 12·9   | " | " | " | 8·85 | " |
| 13·0   | " | " | " | 8·80 | " |
| 13·1   | " | " | " | 8·81 | " |
| 13·2   | " | " | " | 8·86 | " |
| 13·3   | " | " | " | 8·96 | " |
| 13·4   | " | " | " | 8·93 | " |

Broadly speaking then, a rich milk is distinguished from a poor, not only by a higher percentage of fat, but also by a somewhat larger amount of solids not fat.

From the very large number of examinations on which the results are based, it might be inferred that the latter represent the actual average composition of the milk in question. This would undoubtedly be the case if there would be a strict relation between number of samples and quantity of milk. I shall better be able to make myself clear on this point by referring to the system on which the samples are taken. It is the rule to take at least one sample of milk per day from each supplier, morning and evening milk being sampled alternately; and further, on more or less frequent occasions samples from every single churn received from each of the suppliers on a particular day. The quantity of milk is taken into account so far that, as a rule, two samples are taken regularly in case a supplier sends more than five, and three samples in case he sends more than ten churns at a time. When the month is over, the averages are drawn of the analyses of morning milk and of evening milk from every supplier, and the mean between the two returned as the average monthly composition of the milk from that particular source. The average of the figures thus obtained represents the monthly average composition of all the milk received.

Is this mode of calculating the average composition fair—i.e., can and does it give correct results? A first objection which might be raised is that morning milk and evening milk are treated exactly alike, notwithstanding the fact that they are by no means alike. Cows are milked, as a rule, between 5 and 7 o'clock in the morning, and between 4 and 6 o'clock in the afternoon. They give after the longer night interval a larger quantity of morning milk of a poorer, and after the shorter day interval a smaller quantity of evening milk of a richer description. The differences in quantity and quality may be considerable in case the intervals between the two milking times are more dissimilar. Here is an example: Twelve cows had, for some reason, to be milked during a period of ten days at 5 o'clock in the morning, and again at 12 o'clock mid-day. The first meal contained on average 12·15, the second 13·49 total solids; the yields stood in

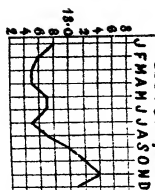


# *Average Composition of 120,540 Samples of Milk--P. Vieth.*

1881

6592 Samples

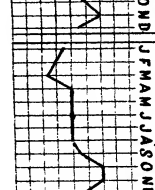
J F M A M J J A S O N D



1882

9190 Samples

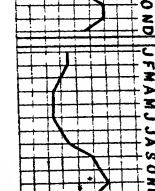
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1883

9650 Samples

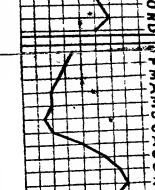
J F M A M J J A S O N D



1884

10399 Samples

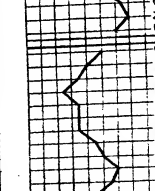
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1885

11889 Samples

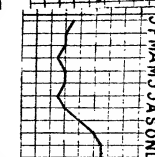
J F M A M J J A S O N D



1886

12181 Samples

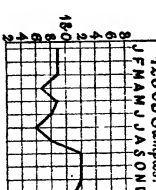
J F M A M J J A S O N D



1887

12663 Samples

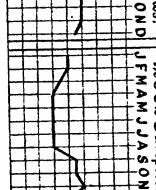
J F M A M J J A S O N D



1888

12682 Samples

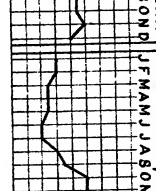
J F M A M J J A S O N D



1889

12617 Samples

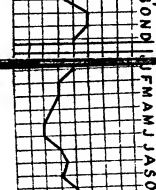
J F M A M J J A S O N D



1890

11816 Samples

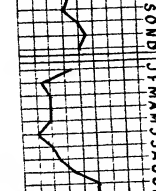
J F M A M J J A S O N D



1891

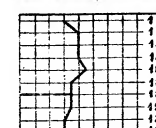
11361 Samples

J F M A M J J A S O N D



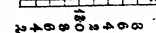
Yearly Averages:

1223 1223 1223 1223 1223 1223 1223 1223 1223 1223 1223 1223



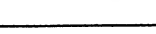
1223

1223



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1223

1223



1223

1223



have shown slight differences on several occasions, and I have good reason to attribute these differences to the unavoidable neglect of the quantities of milk to which the analyses of the former series refer. The differences between the two series, whenever they did occur, were, however, only small; and as they practically disappeared in the yearly averages, the objection on this account may also be laid at rest, and the result, as stated, taken as representing the actual average composition of the milk to which the analyses refer.

So much with regard to the average composition of milk; and now, in addition, a few words with regard to limits, which may be not out of place, although, strictly speaking, they do not fall under the title of this paper. The year 1891 is distinguished by the fact that the quality of milk was lower than usual for fully six months, viz., from February to July. The yearly average is the lowest I have observed since 1880, and so is the monthly average for June. In June there were analysed 1,052 samples, taken from railway churns on their arrival. Among all these samples there was not a single one with solids not fat below the Society's limit, the lowest figure found being 8.70. In one sample the total solids fell below 11.5, viz., down to 11.38. As to fat, the results were less favourable. In fifty-one samples the calculated figures for fat were below 3 per cent., the lowest result being 2.6. As the worst samples came from a few particular farms, it was easy enough to keep the milk back from distribution and work it up for cream. I do not wish to be understood that results as low as some of those just mentioned, and perhaps lower, do not occur in other months; they are occasionally even met with during the time of the year when the highest average composition is observed.

My object in bringing these results under your notice is by no means to raise the cry that the standard adopted by the Society is too high. On the contrary, I think it very judiciously fixed. But in upholding the standard of purity it should not be forgotten that the cows have never been asked for, nor given their assent to it, and that they will at times produce milk below standard. A bad season for hay-making is, in my experience, almost invariably followed by a particularly low depression in the quality of milk towards the end of winter. Should the winter be of unusual severity and length—as was the case last year—the depression will be still more marked. Long spells of cold and wet, as well as of heat and drought during the time when cows are kept on pasture, also unfavourably influence the quality, and, I may add, quantity of milk.

I have on several previous occasions expressed my opinion, and should like to repeat it once more, that whenever the law should be altered, it would be highly desirable to word it so as to allow to condemn a milk, not “because it is adulterated,” but “because it is below a legally fixed standard.” This need not necessarily exclude prosecution in cases where adulteration can be proved, although the milk is still above standard.

The highest monthly average was, in 1891, as indeed in almost every year, that for November. In this month there were found, among 1,110 samples, forty-three in which

the three items, total solids, fat, and solids not fat, were respectively 14.0, 5.0, and 9.0 per cent. or above.

I have every now and again—more frequently this winter—come across samples with unusually high specific gravities which, to the superficial observer, would suggest abstraction of cream. Such samples have been received for a shorter or longer period of time from well-known dairies, which were absolutely beyond suspicion. Without going further into details, I will give you the complete analysis of one of the samples in question, the specific gravity of which was 1.0363 :—

|            |     |     |     |     |     |                 |
|------------|-----|-----|-----|-----|-----|-----------------|
| Water      | ... | ... | ... | ... | ... | 86.14 per cent. |
| Fat        | ... | ... | ... | ... | ... | 3.62 „          |
| Proteids   | ... | ... | ... | ... | ... | 4.66 „          |
| Milk Sugar | ... | ... | ... | ... | ... | 4.58 „          |
| Ash        | ... | ... | ... | ... | ... | .82 „           |
|            |     |     |     |     |     | <hr/>           |
|            |     |     |     |     |     | 99.82           |

From this analysis it will be seen that proteids, and consequently also ash, are unusually high. My explanation is that the milk was yielded by highly-fed cows which were in the last stage of the period of lactation.

#### DISCUSSION.

Mr. Woosnam suggested that the members should have Dr. Vieth's table framed.

The President thought the suggestion an exceedingly good one. The table was a monument of patient labour and research. They had before them the results of Analysis of 120,000 milk samples, and were able to appreciate the amount of work that had entailed. There could be no doubt, that if it had not been for Dr. Vieth, Public Analysts would not have obtained their present position in regard to milk analysis.

#### REPORTS ON WATER ANALYSIS.

By LEO TAYLOR.

*Read at Meeting, March, 1892.*

The question I have to bring before you this evening, follows almost naturally the paper read by my friend, Mr. Cassal, at the last meeting of the Society. Those of you who were present at that meeting will remember the severe manner in which several processes of water examination and analysis were dealt with. Generally speaking, the tendency of the discussion, I take it, was the upholding of the Society's methods of analysis. It is upon this point I wish to say a few words and ask the assistance of members in putting down, what I consider to be a most injurious practice, and one calculated to place analysts who have public duties to perform, in a false position.

At the outset let me disclaim any personal motives in this matter. I shall have to mention the name of a member of our profession who occupies a very prominent position,

who is many years my senior, and who probably practised water analysis when I was struggling with my alphabet; but I do so simply from motives of duty and because I feel that this course has been forced upon me by the gentleman I refer to.

It has been my privilege for eight or nine years past to act as chemist to the Walthamstow Local Board, and during that time I have analysed a large number of waters, principally from wells, the majority of which I have had to condemn, and the wells have been closed upon my certificate. In making these analyses, I have been guided by the scheme drawn up by the Special Water Committee of our Society, and published in *THE ANALYST* of July, 1881.

The details of my analyses comprised estimation of total-solids, solids non-volatile, solids organic and volatile, chlorine, nitrogen as nitrates, poisonous metals, hardness, oxygen reqd., saline and organic ammonia; physical examination as to appearance in 2-ft. tube, taste, smell, suspended matter and behaviour of solids on ignition. Upon the results of this examination I based my report and expressed an opinion as to the value of the water from a hygienic point of view.

In the early part of last year I was instructed to investigate the character of the East London Company's supply to Walthamstow, and it was found, during the seven months over which the sampling extended, that the quality of the water varied considerably in different parts of the town. Upon the quality of the samples it is not my intention to touch, as that has nothing to do with my subject to-night; but it was necessary for me to have gone thus far into detail in order that you may understand my position and the letters I am about to place before you.

The results of this investigation, together with my remarks upon each sample, were tabulated by the Medical Officer of Health of the district, and copies distributed to various authorities, amongst whom was Dr. E. Frankland, as official adviser to the Local Government Board.

The acknowledgment of Dr. Frankland's was in the following terms:—

THE YEWS, REIGATE HILL,  
SURREY, *January 9th*, 1892.

DEAR SIR,

*East London Company's Water.*

I am in receipt of your letter of the 5th inst., and enclosure and in reply, have to say that the analyses given in the Report of the Medical Officer of Health are not complete. *They give no information regarding the quantities of organic elements in the samples; and failing these data it is impossible to form any trustworthy opinion as to the quality of the water from a hygienic point of view.*

I report monthly to the Local Government Board on the quality of the East London Waterworks Company's supply from (1) the river Lea, and (2) from deep wells in the chalk, the various wells being in turn submitted to investigation.



In December last, nearly all the river water delivered in London was of very inferior quality; but, *as a rule*, the river supply of the East London Company compares favorably with the waters derived from the Thames, whilst their supply from deep wells is invariably of excellent quality.

I am, DEAR SIR,

Yours truly,

E. FRANKLAND.

GILBERT HOUGHTON, Esq.,

*Clerk to the Walthamstow Local Board.*

The statement contained in this letter was so extraordinary and far-reaching, imputing that all my water work for the Board had been valueless, and in fact opening up all sorts of legal questions as to the power of closing wells, &c., that the letter was submitted to me for consideration and report.

I replied to it as follows:—

BEACHFIELD, WALTHAMSTOW,  
*January 14th, 1892.*

DEAR SIR.

I have seen the letter received by you from Dr. Frankland, and am surprised to notice in the first part of the letter Dr. Frankland states that my figures, as appearing in your Medical Officer's Report, are incomplete, inasmuch as the organic elements have not been determined. Dr. Frankland goes even further and says that "failing these data it is impossible to form any trustworthy opinion as to the quality of the water from a hygienic point of view."

I must emphatically traverse these statements absolutely, as entirely unwarranted.

Dr. Frankland has here committed himself to a statement which is utterly at variance with the opinions held by almost every chemist but himself.

Some years ago, the Society of Public Analysts appointed a Committee to investigate the question of Water Analysis, and a scheme was drawn up by that Committee, which has since been adopted by almost every analyst. The analyses I have had the honor to submit to your Board have all been worked upon the lines laid down by that scheme.

The combustion process of water analysis, or as it is more generally termed, the "Frankland" process, was invented by Dr. Frankland and has been tried and abandoned as too cumbersome and unwieldy for general use. Very few chemists even profess to use it.

This is not the time to enter into a discussion as to the relative value of the two processes, but I contend, and it has been proved beyond dispute, that either the "Frankland," or the "Wanklyn" process, in competent hands, will enable the same opinion as to the quality of a water to be arrived at. Therefore it is as wrong to say that a water cannot be judged from my figures, as it would be to say that Dr. Franklands'

analyses are incomplete and valueless, for want of the saline and organic ammonia determinations.

The latter part of Dr. Frankland's letter practically confirms my reports, the last sample which I examined being taken at the end of November.

The statement that "*as a rule* the river supply of the East London Company's compares favorably with the water derived from the Thames," goes for nothing, as he does not say that in December it *did* compare favourably; moreover, if it did, then it would only be equivalent to saying that the East London supply was the best of a very bad lot.

Acknowledging, as I do, the good qualities of the supply to the East side of the town, I feel that any samples to be examined must be taken without notice to the Water Company, because it would doubtless be a simple matter to supply the whole district with the better water while the samples were being taken.

In many of the districts served by the metropolitan Companies, the local authorities have instructed their analyst to periodically examine the water supply, as it has been found impossible to keep the Companies up to their duties without such supervision. The official analyses reported monthly (I refer to those signed by Messrs. Crookes, Odling and Tidy), are done *on behalf of the Companies*, and not for the Local Government Board, as is generally supposed, and do not therefore have the same value as independent analyses such as your Board instituted last year.

I remain, DEAR SIR,

Yours faithfully,

LEO TAYLOR.

GILBERT HOUGHTON, Esq.,

*Clerk to the Walthamstow Local Board.*

The Board was apparently satisfied with this reply, and wrote Dr. Frankland that the report on the water supply had been sent to him for his information only, and asking him if, in the discharge of his official duties, he would occasionally take East London Company's water from each end of the town and so embrace the different supplies.

To this Dr. Frankland replied, regretting that his arrangement with the Local Government Board did not allow his undertaking the collection and analysis of samples from the Walthamstow district, but he expressed his willingness to examine, under certain conditions, samples sent to him, and to include the reports on these in his monthly reports on the Metropolitan Water Supply. These conditions included the payment of a certain fee which need not be mentioned here.

There the matter rests at present. I do not fear that future samples will find their way to Reigate, instead of remaining in Walthamstow, but what I do fear is, that this suggestion of incompetence may make itself felt in other quarters where the analyst may not have the same confidence reposed in him that fortunately obtains in my case,

and therefore ask that some expression of opinion may be given upon this old and much debated question.

I have recently gone through much of the literature bearing upon the water fights in bygone years, and have been reminded of the exciting discussions, at some of which I was present, in this room. I do not anticipate that such times will come again, because I feel sure the almost unanimous feeling of analysts is against the organic carbon and nitrogen process, and it seems like raking up an old bogey to bring such a matter before you in the Year of Grace, 1892. The necessity for it, however, has arisen, and with a young member like myself, I could have wished a more prominent man should have brought the matter to your notice, but that in the nature of things is impossible, because I do not think the remarks against which I have been forced to protest would have been dared to have been made against a better-known chemist.

#### DISCUSSION ON MR. LEO TAYLOR'S WATER ANALYSIS.

Mr. Alfred H. Allen said he thought that Dr. Frankland had no right to force upon a brother analyst, who happened to be junior to him, or rather upon the clients who employed him, a particular method which he was perfectly well aware was not used by one analyst in a hundred. It had been well said that nothing more easily found its level than an analytical process. He was not prepared to suggest that it was justifiable to condemn a water only examined either by the Frankland or Wanklyn process, or any other process. He thought the whole of the results obtained should be taken into consideration. He thought it very important to have an estimation of the organic nitrogen, and any process which would do that was worth consideration.

Mr. Cassal thought there could be little doubt that if it were officially possible for Dr. Frankland to withdraw the letter referred to he would willingly do so. Dr. Frankland, as well as the analysts employed by the Water Companies, had, perhaps, been somewhat harried lately. There had been representations from different parts of London, pointing out the impure nature of the water supplies; several special samples had to be taken; and it was, perhaps, somewhat awkward that the analysts who made the first analyses, viz., those for the local authorities, and who had found that the waters were dirty, had to be agreed with in their conclusions. The sentence in Dr. Frankland's letter was certainly an unfortunate one, and it would be said by many that, from a professional point of view, it would have been far better if it had not been written. Dr. Frankland had said that Mr. Taylor's report gave no information concerning the quantity of organic elements, meaning thereby "organic carbon and nitrogen," in the samples, and failing these data, that it was impossible to certify upon them. It was quite impossible for Dr. Frankland to maintain such a position at the present day. Hardly any analysts in this or any other country had adopted the process used by Dr. Frankland. This matter again raised one of the points which he (Mr. Cassal) had brought before the Society at the last Meeting, and which had been, to a certain extent, discussed, viz., as to the advisability of giving

analytical details in reports on water. Mr. Taylor's case afforded an additional example of the evil resulting from the custom prevailing among analysts of giving analytical details in their reports. The question of water was a difficult one to deal with. It was doubtful, he thought, whether, in the case of water, the giving of analytical details could at present, and for some time to come, be avoided; but that it was originally wrong to do so, there could not be the slightest doubt. Mr. Taylor had simply followed the usual practice, and had given the results of the processes recommended by the Society. He, therefore agreed with the President in thinking that Mr. Taylor was entitled to the protection of the Society—at any rate to its official countenance—and, no doubt, it would be extended to him. He (Mr. Cassal) had, some time ago, condemned certain samples of water delivered by two of the London Companies as being dirty and insufficiently purified for a public supply. Dr. Tidy had taken the opposite view, and in the course of his report had referred to the analytical results. Dr. Tidy objected to the statement of results in parts per hundred thousand and parts per million, because he (Dr. Tidy) preferred grains per gallon, and took occasion to remark that a fraction of a "grain" was not worthy of consideration. That instanced the danger alluded to. Mr. Cassal held that the best course to adopt was simply to traverse such statements whenever they were made. He understood that Mr. Taylor had done this, and if so, his position was a strong one.

Mr. Bernard Dyer said that reference had been made by both Mr. Taylor and Mr. Cassal to the desirability of stating results in some uniform way; and reference had been made to the fact that the Society, some years ago, appointed a Water Committee which sat for a long time, and which drew up a scheme for the regulation of water analysis. He thought that it was a great pity that while some members adopted the processes for water analysis recommended by the Society, they nevertheless disregarded the Society's views as to the desirability of unanimity in the mode of stating results. Referring to a report which Mr. Taylor had laid on the table, he pointed out that, instead of stating all his results in grains per gallon, which was the way in which the Society of Public Analysts, in adopting the Water Committee's Report, suggested that they should be stated, Mr. Taylor (like, he regretted to say, many other analysts) put down his results in what he would forgive him for calling "a miserable hash up" of grains per gallon and parts per million. He thought it was highly desirable that, if figures were to be given at all, chemists should be agreed as to some definite way of recording them.

Mr. A. H. Allen suggested that the original report of the Water Committee, which had been referred to, should be reprinted by the Society at a price which would cover the cost; and that additional information, in regard to alternative processes, might be advantageously added.

Mr. Dyer, replying to Mr. Allen, said that enquiries had often been made for copies of the old water scheme, but it had been out of print for a long time. He thought it would be desirable to re-print the scheme. He had a very vivid recollection of the labours of the Water Committee, and he was not anxious to see another Water Committee

appointed to revise the scheme; but it might be possible to make some additions or suggestions. It would have to be carefully done.

Mr. W. Thomson thought that it would be advisable to reprint the pamphlet. He suggested that the Water Committee should be re-elected, and should re-consider the matter.

Mr. Cassal failed to see that, because some ten years ago, a committee of the Society of Public Analysts suggested that results of water analyses should be stated in grains per gallon, Mr. Dyer should wish to bind Mr. Taylor rigidly to the grain per gallon method. It was an obsolete method, and scientific men of the present day no longer used such measurements.

**On the determination of Amyl Alcohol by Röse's method. A. Scala.** (*Gazzetta Chimica Italiana*, 1891—346.)—The author reviews the previous investigations on the presence and amount of higher alcohols in fermented liquids, and gives a fairly complete list of the results of different observers.

In 1886, Röse (*Ber.* 1887—113), published a method of estimating the higher alcohols, founded on the property of chloroform to increase in volume directly as their quantity in a spirit. He employs a stoppered tube 20 m.m. in diameter, and 45 to 50 c.m. long, enlarged at the upper part, graduated from 20 to 45 c.c., and holding in all 175—180 c.c. Into this tube he measures exactly 20 c.c. of chloroform, previously purified and distilled, and 100 c.c. of the spirit to be examined which must contain 50 per cent. of alcohol by volume. The tube is closed and cooled to 15° C. in a vase of water for half-an-hour, then shaken vigorously for two minutes and replaced in the vase to allow the chloroform to settle; the tube being rotated between the fingers and gently shaken at the same time to assist the drops to descend. After a hour's repose at 15° C. the tube is read; 1 volume per cent. of amyl alcohol increases the volume of the chloroform by 2 c.c. The experimental error is 0.05 c.c.

Stutzer and Reitmar (*Centralb. f. allgm. Gesund. Hef. II.* 3, 191), modify the process by using 1 c.c. of sulphuric acid of 1.286 sp. gr., and by making their alcohol of 30 per cent. strength. They find that 1° C. of temperature makes a difference of 0.1 c.c. in the volume of the chloroform. Their mode of operation is as follows: Distil 200 c.c. of brandy or other spirit with several drops of caustic potash solution until four-fifths have passed over; make up the distillate to 200 c.c.; determine the specific gravity, calculate and add the quantity of water necessary to obtain a solution containing 30 per cent. by volume of alcohol; 100 c.c. of this alcoholic solution, 20 c.c. chloroform, and 1 c.c. of sulphuric acid are then treated as in Röse's method.

Sell (*Arbeiten. aus. d. Kais. Gesdh. Vol. IV.*, 1888), published a comparison of Röse's method with the two due to Traube (capillarimetric and stalagimetric), and gives the preference to the former; he gives two corrections that may be used in working,—1, a difference of 1° C. makes a difference in the volume of the chloroform of 0.26 c.c., and

2, an error of 1 per cent. by volume in the alcoholic solution makes a variation in the volume of the chloroform of 0.30 c.c.

Bardy (*Journ. Pharm. et Chimie.*, Vol. XVIII.), confirms Sell's preference, but uses a larger apparatus.

Fresenius (*Zeits. f. Anal. Ch.* 1890—307), expresses an opinion that spirits (cognac, rum, arrack) may contain a substance which has a contrary effect to amyl alcohol, *i.e.*, diminishes the increase of the volume of the chloroform.

In the author's experiments the alcohol used was the purest absolute alcohol of Kahlbaum, distilled from lime, and was brought to the exact density corresponding to 30 per cent. by volume in Hefner's tables: the chloroform was purified by Marquardt's method, *i.e.*, 200 c.c. of chloroform were heated with 3.5 gms. of potassium bichromate, 1.5 gms. sulphuric acid, and a little water in a closed bottle to 85° C. for 6 hours; the chloroform was then distilled, shaken with barium carbonate, being warmed at the same time of the water-bath, again distilled, dried with calcium chloride, and finally re-distilled ready for use.

The following are the details of manipulation:—Wash the tube with strong sulphuric acid, then with nitric acid, and finally well rinse with water to remove all acid; completely dry the apparatus by warming and blowing air through it and place it in a support. With a long-stemmed funnel pour in a little more than 20 c.c. of chloroform, and place the tube in a bath kept at 15° C. When the volume of the chloroform is constant, take out the excess with a long fine tube, and leave exactly 20 c.c. Place also in the bath the alcohol to be tested (at 30 per cent. volume strength) and some sulphuric acid of 1.286 sp. gr. Without removing the tube from the bath, measure in 100 c.c. of the alcohol, and 1 c.c. of sulphuric acid; stopper the tube, take out of the bath, invert and shake it about 120 times; again turn and place it in the bath to settle, gently rotating from time to time to assist the deposition of the drops clinging to the sides, and read the volume of of the chloroform after 20 minutes.

An apparatus graduated in  $\frac{1}{20}$  c.c. is found to give the most exact results, it being possible to read to 0.01 c.c. If the graduation be finer, the bore is so narrow as to present inconveniences.

*Base.* By the *base* is meant the volume assumed by 20 c.c. of chloroform when shaken with 100 c.c. of the purest 30 per cent. by volume alcohol; this differs with various samples of chloroform, and should be determined for each; results in the paper are given showing from 21.35 c.c. to 21.65 c.c. for different chloroforms; with the same sample it is constant, and can be determined to 0.01 c.c.

The specific gravity of the alcohol is an important factor and must be determined accurately; a difference of  $\pm 0.0001$  makes an error in the reading of the volume of the chloroform of  $\mp 0.0235$  c.c.

A difference of temperature of  $1^{\circ}$  C. increases or diminishes the volume by 0.036 c.c.

*Calculation of impurity.* 1 c.c. of each of the following substances increases the volume of the chloroform over the base as follows:—

|                      |     |     |            |
|----------------------|-----|-----|------------|
| Aldehyde             | ... | ... | 0.200 c.c. |
| Paraldehyde          | ..  | ... | 1.000 „    |
| Furfurol             | ... | ... | 0.601 „    |
| Propyl Alcohol       |     | ..  | 0.502 „    |
| Normal butyl Alcohol |     |     | 1.161 „    |
| Iso—butyl            | ... | ... | 0.949 „    |
| Amyl                 | ... | ... | 1.507 „    |
| Essence of Aniseed   | ... |     | 0.588 „    |
| „ „ Cinnamon         |     |     | 0.750 „    |

The author prefers to calculate the increase as amyl alcohol, because it is the most important constituents of fusel oil, and also because the error caused by other impurities is not likely to be very great owing to their smaller co-efficients.

He gives the following table: —

| Increase in vol.<br>of Chloroform. | Quantity of<br>Amyl Alcohol. | Increase in vol.<br>of Chloroform. | Quantity of<br>Amyl Alcohol. |
|------------------------------------|------------------------------|------------------------------------|------------------------------|
| 0.01 c.c.                          | 0.0063 c.c.                  | 0.1 c.c.                           | 0.0634 c.c.                  |
| 0.02 „                             | 0.0127 „                     | 0.2 „                              | 0.1268 „                     |
| 0.03 „                             | 0.0190 „                     | 0.3 „                              | 0.1910 „                     |
| 0.04 „                             | 0.0254 „                     | 0.4 „                              | 0.2535 „                     |
| 0.05 „                             | 0.0317 „                     | 0.5 „                              | 0.3169 „                     |
| 0.06 „                             | 0.0380 „                     | 0.6 „                              | 0.3802 „                     |
| 0.07 „                             | 0.0444 „                     | 0.7 „                              | 0.4436 „                     |
| 0.08 „                             | 0.0507 „                     | 0.8 „                              | 0.5069 „                     |
| 0.09 „                             | 0.0571 „                     | 0.9 „                              | 0.5702 „                     |
|                                    |                              | 1.0 „                              | 0.6336 „                     |

Determinations may be made with almost equal exactitude at temperatures other than  $15^{\circ}$  C. taking as *base* the volume of chloroform after shaking with pure alcohol at that temperature.

The author discusses the value of the results obtained, and shows that while alcohol (spirit of wine) contains usually less than 0.2 per cent. by volume of amyl alcohol, brandies contain over 2 per cent. by volume.

He concludes that the method of Rösé is the most exact for the determination of amyl alcohol in spirits, but does not consider that the results of the determinations give much information. He hopes that in the future they may be more useful. H. D. R.

**The Valuation of Commercial Aluminium.** A. Rossel. (*Schweiz. Wochenschr. Pharm.* 1891, xxix. 471, through *Chem. Zeit.*)—The impurities present in commercial aluminum consist almost exclusively of silicon and iron. Both affect the value of the material considerably. The author reviews the usual methods which leave a good deal to be desired, and recommends the following process. About three to four grms. of aluminum are weighed out and dissolved in about 35 c.c. of warm caustic potash solution, containing 30–40 per cent. of KOH. A black flocculent residue is left. The solution is made acid with hydrochloric acid, without previous filtration and evaporated to complete dryness in a platinum basin. The residue is taken up with hydrochloric acid and the silica determined as usual. The iron is determined by dissolving a similar quantity by the same method, adding sulphuric acid in excess, and titrating with permanganate. Special attention should be paid to the necessity of having the caustic potash free from silica.

B.B.

**The Weighting of Leather.** B. Kohlmann. (*Chem. Zeit.* 1892, xvi. 16-17.) Samples of leather, the weight of which has been increased by illegitimate means, are by no means uncommon. As the price per kilo of a good leather is about three shillings, the practice is not unprofitable. Insoluble inorganic substances are seldom used for this purpose, because they, of necessity, remain on the surface and are easily recognised. The commonest adulterants appear to be sugar, barium salts, and worthless vegetable extracts. The literature on the subject is very scanty, and data must be compiled from the examination of genuine samples to determine the limits beyond which adulteration may be considered proved. All samples should be dried at 105° C., as the quantity of water varies between 12–20%. Experiments on pure leather showed that the dry substance contained 10–12% of matter soluble in water, and 0.5–1.0% of ash. Sugar and barium salts were not present. In testing leather it must be remembered that the excess of tannic acid, which is always present in good samples, yields sugar by the action of alkalies, and therefore an aqueous extract reduces an alkaline copper solution, such as Fehling's solution. The method adopted by the author consists in extracting a weighed portion of the sample, cut into thin strips, by repeated treatment with cold water, precipitating the tannin with lead acetate, removing the excess of lead with sodium carbonate, and determining the sugar in the filtrate by Fehling's solution, or by the use of the polarimeter.

The following table shows some of the results obtained :—

| No. of Sample                        | ... | 1        | 2    | 3        | 4    | 5        | 6    | 7        | 8        |
|--------------------------------------|-----|----------|------|----------|------|----------|------|----------|----------|
| Organic matter insoluble in water... | %   | 79.9     | 89.2 | 79.8     | 78.0 | 73.6     | 87.7 | 80.0     | 77.6     |
| Organic matter soluble in water      | ... | 15.9     | 10.2 | 15.8     | 20.9 | 22.6     | 11.8 | 17.1     | 19.3     |
| Ash                                  | ... | 4.2      | 0.6  | 4.4      | 1.1  | 3.8      | 0.5  | 2.9      | 3.1      |
| Sugar                                | ... | Present. | Nil. | Present. | Nil. | Present. | Nil. | Present. | Present. |
| Barium                               | ... | "        | "    | "        | "    | "        | "    | "        | "        |



It therefore appears that only 2 and 6 are pure. Of the remainder, five contain both barium salts and sugar, and one (No. 4) is adulterated with soluble organic matter, while the ash is higher than is normal.

B. B.

**Compressed Yeast.** (*British and Foreign Confectioner.*, vol. xvii., p. 194.) Mr. J. Kirkland, in a lecture on Baking, delivered at the Heriot-Watt College, Edinburgh, states "For a long time it was considered impracticable to press yeast without the addition of starch, so that it would keep. This notion, which at best was but a superstition, is now exploded, and some of the large manufacturers have stopped making "mixed" altogether."

W. J. S.

**Gravimetric Estimation of free Sulphuric Acid.** M. Weinig. (*Zeit. f. angewand. Chemie.* 1892, p. 194). Free sulphuric acid can be determined in a similar manner to that proposed by Schaffgotsch for estimating free nitric acid, namely, by the addition of a slight excess of ammonia solution, evaporating, drying, and weighing the residue. The ammonium sulphate crystallizes water-free, melts at  $140^{\circ}\text{C}$ ., and decomposes at a higher temperature than this; it can therefore be safely dried at  $115^{\circ}$  to  $120^{\circ}\text{C}$ . For the preparation of a standard solution of sulphuric acid, a certain number of c.c. of the diluted acid are pipetted into a tared platinum dish, about half a c.c. of pure ammonia solution added beyond the point of neutralisation, the solution evaporated to dryness, heated for half an hour to  $120^{\circ}\text{C}$ ., cooled in the exsiccator, and weighed. A simple calculation gives the amount of sulphuric acid contained in the quantity of dilute acid used in the experiment. The addition of too large an excess of ammonia is to be avoided, or spurting takes place during the subsequent evaporation.

W. J. S.

**Soapy Milk.** F. J. Herz. (*Mitt. Milchv. Vereins im Allgau*, 1892, vi. 9, through *Chem. Zeit.*). Samples of milk which were suspected of being skimmed on account of their high specific gravity ( $1.0351$ – $1.0365$  at  $15^{\circ}\text{C}$ .), were found to have a content of fat of  $3.7$ – $6.08\%$ , while the specific gravity of the whey of the spontaneously curdled milk was  $1.0313$  in one instance, the fat of the same sample being  $5.03\%$ , and the solids not fat, calculated by Fleischmann's formula,  $10.04\%$ . In other cases, the values similarly arrived at were  $10.05$ ,  $10.21$ ,  $10.25$  and  $10.26\%$ . It therefore appears that Fleischmann's formula is inapplicable to these abnormal samples. The author adopts the term "soapy milk" for such samples because they possess a soapy smell, and maintain a persistent froth for as long as 24 hours. The smell is not apparent in the fresh milk, but is developed after it was stood 24–36 hours. On treating such milk with potash a fishy smell is produced, instead of the usual odour, recalling that of trimethylamine. The froth or scum on the milk is distinguished from that which forms on ordinary milk, in that it does not consist of tangible floating particles, and cannot be filtered off. "Soapy" milk shows

little tendency to curdle. Three samples, kept for 24 hours at 40° C. and then exposed to the ordinary temperature of the room, with free access of air and occasional shaking, took, in two cases, eight days and in the other twelve days, to curdle. Apart from its disagreeable taste and smell, "soapy" milk is troublesome to use in butter and cheese-making. The reason for this abnormality, which does not seem to depend on the period of lactation, and has been observed in well-fed cows, has not yet been detected.

B. B.

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**Drouot's Apparatus for the Examination of Butter.** In 1887, F. Drouot (*Industrie Laitière*, 1887, 28, 285) introduced an apparatus for distinguishing artificial butters and mixtures from genuine butter.

The essential part is a little table of tin-plate 27 cms. by 7 cms. containing 6 hemispherical cups of about 32 m.m. stamped in it, a thicker iron plate of the same size with two handles at either end, and a spirit lamp to heat it.

This plate is first heated to about 60°C., and then placed over the little tin plate, in the cups of which are placed the samples to be examined (about 1.5 grains in each cup); the iron plate should be just so hot as to melt the samples in about 5 minutes, at the expiration of which time the aspect of the samples should be noticed. Genuine butter appears as a clear oil, with a layer of white liquid at the bottom, but margarine is always turbid, more or less opaque, and does not deposit a sharp coherent layer on the bottom. Mixtures give characters between the two.

The reflecting surface of the cups materially aids the observation.

Overheating is to be particularly avoided, as even undoubted margarine may thus become clear.

Besana (*Sui metodi atti a distinguere il burro artificiale dal burro naturale*. Lodi, 1888) gives a very favourable opinion of the method; all genuine samples gave clear liquids, except a very few butters obtained by shaking, which gave a very slight turbidity. Rancid butter cannot be tested by this method, unless great care be taken in removing the outer layers, and using only the centre portion.

Wolny (*Milch Zeitung*, 1887, 32, 658) confirms the author's statement that 10 per cent. can be detected by the Drouot apparatus, but Ravà (*Annuario d. R. Staz. Sperim. di Lodi*, 1887, 136) and Salvatori (*Staz. Sperim. Ital.*, 1888, xiv., 516) fix the limit of certainty at 20 per cent., and express themselves unfavourable to the apparatus for the detection of small mixtures.

The "Congress of Directors of the Italian Royal Agricultural Stations and Royal Agricultural Laboratories" recommends this method as a preliminary one, and the French "Society for the Encouragement of the Dairy Interests" awarded a gold medal to the author.

H. D. R.

# THE ANALYST.

JUNE, 1892.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A meeting of the Society was held on Wednesday, the 4th of May, the President (Mr. Hehner) in the chair.

The minutes of the previous meeting were read and confirmed.

The following gentlemen were proposed as Members:—Mr. James William Westmorland, F.C.S., A.R.S.M., Analytical Chemist, 2, City Road, London, E.C.; Mr. Samuel Francis Barford, F.I.C., Member of the Pharmaceutical Society, Member of the Society of Arts, "Eastleigh," Queen's Road, Leicester; and Messrs. G. H. Gabb and W. N. Yarrow, assistants to Mr. A. W. Stokes, were proposed as Associates.

The following gentlemen were duly elected Members of the Society:—Percy Gerald Sanford, F.I.C., F.C.S., Analytical and Consulting Chemist, 20, Cullum Street, Fenchurch Street, E.C.; Mr. Harry Silvester, F.I.C., F.C.S., Analytical Chemist, Holyhead Road, Handsworth, Birmingham; Mr. L. J. de Whalley, B.Sc. (London), Analytical Chemist; and Mr. Thos. Shortridge Tweedie was elected an Associate.

Mr. Harvey temporarily occupied the chair while the President read the following papers:—

### NOTES ON BUTTER.

BY OTTO HEHNER.

IN the last number of THE ANALYST, reference is made to an observation which must have struck every analyst, namely, that whilst, as a rule, genuine butters when carefully melted, yield a fat which is practically clear, margarines and badly-adulterated samples melt very turbid.

I have for about a year past kept a record of most of the butter samples which have passed through my laboratory, and have noted the appearance on melting the samples in the water-oven, also the fact, whether preservatives were found or not, together with the result of the analysis.

370 samples have thus been examined with the following results :—

- 162 melted clear, and were genuine.
- 61 melted turbid, and were genuine.
- 81 melted turbid, and were adulterated.
- 66 melted clear, and were adulterated.

Of the 370 samples, 214 were preserved with borax or with boric acid, namely 119 genuine samples, or 53 per cent. of all genuine samples; and 95 adulterated ones, or 65 per cent. of all adulterated samples.

It is obvious from the above table, that while the majority of genuine samples, namely, 72·6 per cent., melted quite clear, and the majority, 55·1 per cent., of the margarines more or less turbid, nothing but the vaguest conclusions can be drawn from the appearance on melting. It is true, that in most cases in which the samples melted clear and yet were adulterated, the percentage of the admixture was comparatively small, say under 20 per cent. But I have met with adulterated samples containing 25, 30, 40, and even 94 per cent. of margarine, and yet they melted clear. These are isolated instances, but they remove the method quite out of the list of reliable ones.

I am not in a position to criticise the statements made by Drouot, Besana, and Wollny,\* who all operated with a little apparatus devised by Drouot, whilst I simply melted my samples in a small beaker at the temperature of the water oven, but my results will be sufficient to make analysts cautious before placing reliance upon such a test.

The general use of boric preservatives should be noted.

#### NOTE ON THE LEFFMANN-BEAM METHOD OF DETERMINING FAT IN MILK.

BY OTTO HEINER.

DRS. LEFFMANN AND BEAM have been kind enough to send me one of their centrifugal machines for the rapid estimation of fat in milk. I have made a few estimations of fat by means of this machine and give the results in the following table :—

|    | Fat by Coil. | Fat by Centrifugal. |
|----|--------------|---------------------|
| 1. | 3·89         | 3·87                |
| 2. | 2·51         | 2·54                |
| 3. | 3·34         | 3·27                |
| 4. | 3·32         | 3·27                |
| 5. | 2·60         | 2·45                |
| 6. | 1·85         | 1·76                |
| 7. | 3·18         | 3·10                |

The results, as far as it is possible to judge from so limited a number of determinations, are therefore quite as accurate as claimed for them by the authors of the process. I find one minute's whirling quite sufficient to separate the whole of the fat. It is there-

\* See abstract, ANALYST, vol. xvii., p. 100.

fore possible, by taking the specific gravity and the fat by the Leffmann-Beam process, to obtain an accurate milk analysis in a very few minutes, using Richmond's and my formula for the calculation of the total solids, or Richmond's slide rule.

I have not yet had time to investigate the exact *rationale* of the method, which is evidently not quite as simple as may at first appear. 15 c.c. of milk are taken, 3 c.c. of a mixture of equal parts of strong hydrochloric acid and of fusel oil are added, and then strong sulphuric acid up to the neck of the little bottle belonging to the machine. After careful mixing, so that all caseine has dissolved, hot dilute sulphuric acid is added up to the zero point of the graduation. Each division of the graduation corresponds to 0.15 c.c. or to 0.1 per cent. by volume of fat. The figure thus obtained is to be multiplied by 0.86; this is, however, not the specific gravity of the butter fat, which when read off is but little above its melting point. I presume the figure is one ascertained empirically, as the fat, after separation from the acid liquor beneath it, smells strongly of fusel oil, and is evidently not pure milk fat, but a mixture.

#### DISCUSSION.

Mr. Alfred H. Allen thought that the graduation of the tubes was based on the fact that 0.86 was approximately the gravity of milk fat at 100° centigrade, but with a substance with so high a co-efficient of expansion as butter fat, even a moderate alteration in the temperature would, he thought, materially affect the volume registered. He would like to know whether Mr. Hehner had made the experiment with water instead of milk, and if so whether any fusel oil had risen to the top of the liquid.

The President replied that he had not tried the experiment.

Mr. Allen, continuing, said that it was difficult to follow the reasoning which led to the adoption of an arbitrary process. The inventor began by taking 15 c.c. of milk; and then added a mixture of hydrochloric acid and fusel oil. He presumed the acid was used to obtain the fat in a kind of emulsion, and on then adding sulphuric acid the fusel oil was dissolved and the fat readily separated from the very dense liquid. It was also quite clear that any centrifugal apparatus would act better with two liquids of different densities, than if they possessed nearly the same density. The inventor could scarcely get very close or accurate results, unless he paid attention to the temperature at which he measured the fat, which could be very easily done by placing the tube in boiling water before observing the volume of the fat. The process described was an arbitrary process; but if it was really butter which came to the top, and not butter fat, *plus* fusel oil (which might be the case), it would be possible to confirm the result by the Werner-Schmidt process, and at the same time have a very useful preliminary indication of the amount of fat. In his opinion, the centrifugal plan ought to be capable of being very extensively applied for the separation of liquids, and had, in fact, been recently applied to that purpose by Mr. Thorner.

Mr. H. Droop Richmond pointed out that if the factor 0.86 was probably obtained by dividing 0.89, the density of butter fat at about 50° or 60° by 1.032 the density of

milk, the use of this factor would correct volume readings to weight percentages. He thought that the error caused by the contraction of the fat, owing to cooling, would be practically negligible and would fall within the unavoidable experimental error.

Mr. A. W. Stokes wished to ask whether the President had found that the fat rose by itself, because he (Mr. Stokes) had tried an experiment in a different sized glass, and he had found that casein rose from below and mixed with the fat, and the results were difficult to read off. Could the fat be read off accurately?

Mr. Woosnam wished to ask if Mr. Hehner had tried leaving the acid upon the milk for any length of time, to see if it had then any effect upon the percentage of butter fat; or whether, in order to get an accurate result, it was necessary to proceed at once with the "whirling" in the machine? Were there any black, solid particles left in the sulphuric acid mixture?

Mr. Hehner, in reply, said that he had not tried the experiment of leaving the acid in very long, because he had found from the few experiments made, that it was more satisfactory to perform the experiments at high temperature, and not to wait till the apparatus cooled down. In reply to the question asked by Mr. Stokes, he stated that if the experiment were properly done, there was absolutely no emulsion between the acid and the fat.

The President having resumed the chair, Mr. Allen read the following paper:—

### ON THE PROPORTION OF WATER IN BUTTER.

By ALFRED H. ALLEN.

A good deal of interest is attached at present to the proportion of water which may be properly contained in butter, in consequence of the sudden appearance in the market of butters containing an unusually large percentage of water. In the years 1877 and 1878, the West Riding officials submitted to me several samples of butter which were found on analysis to contain large proportions of water. Thus I certified to 19·83, 22·24, and 25 per cent. respectively. Action was taken on my certificates and convictions obtained. Since that time, until quite recently, of the thousands of samples of butter which have passed through my hands, hardly any have contained a marked excess of water. It would scarcely have escaped notice in the ordinary process of preparing the butter-fat, and, in fact, the recent cases have forced themselves on my attention during the ordinary process of analysis, there being no previous suspicion that an abnormal proportion of water was present.

The first case among those of recent occurrence was that of a sample, said by the defence to be Cork butter, churned by small farmers from the produce of one or more cows each. On analysis, I certified it to contain 22 per cent. of water, the amount actually found being 22·44 per cent., and added that "In my opinion any proportion of water in excess of 16 per cent. as a maximum should be regarded as an adulteration." Without any evidence being adduced for the defence, it was submitted to Somerset House, when Messrs. Bell, Bannister and Lewin reported that "the sample of butter referred

to in the annexed letter was received here on the 9th inst. (December), securely sealed. We have analysed the butter and declare that it contains 22.98 per cent. of water. We are of opinion that such proportion of water is in excess to the extent, of at least 5 per cent." This certificate is eminently characteristic. It states the minimum adulteration without going further and saying what was the excess of water above the average proportion in butter. It is evident, also, that it fixes the Somerset House limit for water in butter at 18 per cent., and affords one more illustration of the perverse custom of the Somerset House Chemists of straining every point in favour of the defence, instead of occupying the more consistent position of impartial referees of the Court.

On page 64, *et seq.*, of his work on "Food," vol. ii., Dr. James Bell gives results of the analysis of 113 samples of butter, which he says were selected so as to obtain, as far as possible, fair representative samples of butter produced under different conditions; and in the *Report of the Board of Inland Revenue*, 1876, he states that "the samples may be taken as fairly representing the various qualities of butter as made and brought to market by farmers both in England and Ireland. Every care was exercised by the Board's local officers in procuring them, and there can be no question whatever as to their being genuine." I am afraid people who live in the rough world, outside the circle of Arcadian simplicity in which Dr. Bell apparently dwells, will be inclined to think that the Irish peasant-farmer is quite capable of taking, and even likely to take, a wicked delight in supplying an exciseman with an abnormal article. Dr. Bell's remarkable conclusion further presumes that no farmer introduces an excess of water into butter, or makes an addition of foreign fat. This assumption is strictly opposed to my own personal knowledge that margarine is, and has for years past, been habitually bought by dairy-farmers for incorporation in the butter subsequently made and brought to market. He further contends that butter not made for sale must necessarily be genuine, and so practically extends the definition of "genuine" to any butter which has passed through the hands of a careless or incompetent dairymaid, who thereby becomes the arbiter of quality. But Dr. Bell's more recent opinion, as laid down in his work on "Food," vol. ii., page 47, is that "*a greater amount of water in butter than 12 per cent. is unnecessary, so far as attaining a good appearance is concerned, and anything over 16 per cent. is injurious to the keeping qualities of the butter.*" Clearly, it was Dr. Bell's opinion at the time he published his second volume that 16 per cent. is the maximum limit of water to be allowed in butter, in which opinion I cordially concur, but in the modification of his opinion for the guidance of local magistrates, who expect to receive from him impartial advice, he fixes the limit at 18 per cent., and omits all mention of either the average or maximum proportion in well-made butter. This deplorable omission, which is consistent with the usual practice of the Somerset House Chemists, is of course, directly conducive to adulteration.

In the article on "Butter" contributed by Dr. Bell to Thorpe's *Dictionary of Applied Chemistry* (vol. ii., page 300), it is stated that "in commercial butters the water has been found to vary from 4 to about 18 per cent." Here, therefore, Dr. Bell abandons his

position that the exceptional butters included in his 113 commercial samples were "genuine," and again fixes his maximum for water at "about 18 per cent.," which may therefore be regarded as the present Somerset House limit.

There has lately been an organised and systematic attempt, emanating from certain German ports, to place heavily-watered butter on the English market, and hence public analysts should be on the look-out for samples of butter so sophisticated.

In my more recent certificates on watered butter, I have actually quoted Dr. Bell's words, giving him as an authority for the statement that "a greater amount of water than 12 per cent. is unnecessary, and anything over 16 per cent. injurious to the keeping qualities of the butter," and have stated my agreement with that opinion. Such a definite course as this is desirable in the face of the one-sided certificates issued by Somerset House, and of the fact that the solicitor for the defence in a recent case actually contended that *any* amount of water in butter was allowable, seeing that the Legislature had not defined the amount, "finding it impracticable to do so." Such assertions as these are usually made in the absence of the analyst, and if he becomes aware of them, it is only by accident and when the case is at an end; but it behoves public analysts to correct such flagrant misstatements of the scope and purpose of the Sale of Food and Drugs Act.

In 1875, the Society of Public Analysts proposed and adopted for butter the limit of 80 per cent. for butter-fat, leaving 20 per cent. for salt, curd and water. I think this is a perfectly proper limit, but it may be worth while to restate the fact, as I notice that at a recent convention of the American Association of Agricultural Chemists, the Society's limit was erroneously stated to be 85 per cent.\*

In several cases since the one referred to Somerset House, I have met with upwards of 20 per cent. of water in butter, and proceedings have been taken and evictions obtained on my certificates. In one instance the proportion of water reached 29 per cent.!

In proceedings recently taken on my certificate for the sale of butter containing  $21\frac{1}{2}$  per cent. of water, two inspectors from Cork Butter Market were witnesses for the defence. Their evidence was of so startling and novel a character that a short reference to it will not be out of place. They swore that they examined a very large number of samples daily; such a number that the testing of each must have been completed, if I remember their figures rightly, in a fraction of a minute. They observed the taste, smell, colour and consistency of the butter, and were inclined to dispute the analysis, on the ground that butter with so large a proportion of water would not have escaped their attention. They stated that the proportion of water met with in Irish butter sometimes reached 20 per cent; but it did not appear that they had ever actually ascertained the quantity or deputed an analyst to do it for them. They, however, swore that any abnormal proportion of water in the sample was probably due to the weather; for in wet weather the food of the cows was of course wetter, and hence the butter contained more

\* To my astonishment, I find that the S. P. A. limit is incorrectly stated at 85 per cent., in vol. ii. of my "Commercial Organic Analysis."—A. H. A.



water! This novel and highly interesting statement was made in the witness-box. Further, they discriminated between "water in solution" and "water in suspension," but which of these curious forms was the normal, and which the abnormal constituent of the butter, was not made clear.

I find the proportion of water in butter to be most conveniently determined by placing five grammes of the sample in a small tared beaker, and exposing it in an air-bath, to a temperature not exceeding  $110^{\circ}\text{C.}$ , until no more globules of water can be observed on looking at the beaker from below. Generally, the water can be completely expelled in about one hour. The curd and salt can be subsequently determined in the same quantity. After evaporating the water, the fat is re-melted, and filtered into a small beaker kept in the water-oven. The residual matter is rinsed on to the filter with re-distilled petroleum spirit, and washed with petroleum spirit until free from fat. The filter is then dried at  $100^{\circ}\text{C.}$ , and the contents scraped off and weighed. After weighing, the residue, which represents the curd and salt of the butter, may be examined under the microscope for starch, cellular tissue, &c., and then, if desired, treated with cold water, and the solution further examined or titrated with standard silver solution to estimate the salt. Usually, however, it is sufficient to ignite the residue in porcelain at a low temperature, and regard the non-volatile matter as salt, the combustible as curd.

Some butters are far from being homogeneous, and when positive it is preferable to work on 25 or 50 grammes rather than on smaller quantities.

#### DISCUSSION.

The President remarked that lately, with the close competition in the butter trade, when 5% of margarine added to butter made mixing a profitable business, the attention of butter mixers had again been directed to the addition of water. As Mr. Allen had said, having regard to the systematic manner in which butter containing water was forced upon the market by unscrupulous dealers, every per cent. which such men could get recognised by the referees at Somerset House would be a very considerable gain to them and loss to the public. In his opinion, there was no reason why a butter should contain more than 13% of water. When the percentage of water rose above 15 it was either culpably added or negligently left in; and the excess was not only detrimental to the public but to the butter merchants themselves. He had been told by a merchant that, out of a consignment from a particular farmer, out of every hundredweight of butter he lost from 3 to 4 lbs. in transit; whilst, in ordinary butters, the loss was only from one-third to half-a-pound. On analysing a sample of the butter referred to, it was found to contain 18.8 per cent. of what the Irish Inspectors would call "undissolved water."

Mr. Cassal asked what method Mr. Allen used to estimate the water in butter? He wished to ask whether, on melting the samples of butter, the existence of any substantial adulteration with water was rendered evident? He understood Mr. Allen to say that this was so; and if so, it agreed with his own experience.

Mr. Stokes stated that he examined every sample of butter he received microscopically, and his experience was that if a butter contained an abnormal quantity of

water it could be easily seen. Some years ago it was a common occurrence to find large quantities of water in butter and lard ; but of late they had not been nearly so frequent. Under the microscope it could readily be seen whether a sample contained margarine or whether it contained an abnormal amount of water.

Mr. Cassal wished to ask Mr. Stokes whether he relied entirely on the microscopic examination of his samples of butter for the purpose of deciding whether they could be passed or not ?

Mr. Stokes replied in the affirmative.

Mr. Cassal would be glad, that being the case, if Mr. Stokes would give the Society full information as to the method of working. His own impression was that the method was quite unreliable. He would like to know if Mr. Stokes was able to distinguish between a sample of butter which contained from 10 to 12, and one which contained from 18 to 20 per cent. of water by microscopic examination. If so, the results attained were certainly remarkable.

Mr. Stokes expressed his readiness to read a paper before the Society on the subject.

Mr. Allen asked Mr. Stokes if he would at once explain to the Society the way in which he manipulated with the microscope in order to effect this desideratum.

Mr. Stokes replied that he took a butter, just as it came to him, and scraped a large surface clear. He then took a thin layer below this, and placed it on an ordinary microscope slide ; over that he placed a microscopic cover-glass, and pressed this down, so that the butter formed a thin wedge. He now crossed the polarising prisms, so that the field of view was absolutely dark. On placing the slide between the prisms, if there was a trace of butterine or margarine, say within ten per cent., at once a glimpse of light came through. Badly constructed polariscopes let light pass without interposing an object, and are useless for this purpose. In the case of a genuine butter, there was no illumination at all. He had never once found this system fail. No selenite plate should be used, since its results are often delusive.

Mr. Allen replying generally to the remarks made, said that the test mentioned by Mr. Stokes had quite recently appeared in a trade journal, the only variation being that in that paper a plate of selenite was recommended, which he did not gather was the case with the method described by Mr. Stokes. Since that event, he had been asked by butter merchants if he was acquainted with the test. He had replied that he did know it, but that, in his opinion, it was only of value where large proportions of margarine were in question. In a paper recently published in America, it was proposed to dissolve the butter in a drop of oil, and examine it. Since the appearance of the article he had just referred to, he had tried the experiment, and he had found marked double refraction in genuine butters ; and in the case of samples, which he believed to contain margarine in some cases he found double refraction, and in others, none. This caused him to come to the conclusion that there was more to be learnt before the process could be relied on. He would like to endorse what the President had said with regard to the undesirability of giving analytical data in the case of butter analyses. He contended that their clients

had absolutely no right to demand the figures on which they based their opinion as to the presence or absence of margarine; and he had, therefore, declined in recent instances to give them. He was told a few days before the meeting, that a letter written by a German house, contained the statement that "Mr. Allen was entirely behind the age; that he should use the Reichert test, and he would arrive at the same results as other gentlemen." Seeing that he (Mr. Allen), had been among the first to adopt the Reichert distillation process, and recommended it to his brother chemists (ANALYST, x., 103; xii., 11; xiv., 5), and that at a period when the President (Mr. Hehner), doubted its value, even as a sorting test, this allegation was somewhat wide of the mark. But he held very strongly that an opinion on butter should not be based on the result of any single test. There were butters now in the market which were very skilfully adulterated, and it was only by the combined application of several tests that the fraud could be discovered; in fact, to his knowledge, it had escaped recognition in several instances of late. Analysts ought to be very careful not to give to their natural enemies, the adulterators, information respecting the methods they employed for the making of analyses. The discussions at the meetings of the Society were extremely valuable; but when it was known that THE ANALYST was bought regularly by all sorts of people, in order to see what could be done by analysts, and what could not be done, it was evidently extremely undesirable to let the general public know everything they were doing.

Mr. Cassal drew attention to the fact that a note had appeared in the *Times* on the adulteration of Normandy butter; and that it was pointed out therein that science failed entirely to detect certain percentages of margarine in butter, but that a test had now been devised, which was all that could be desired, and which "could be applied by an 'inspector' with the aid of a boy." He received Mr. Stokes' statement with all respect, and he would look forward with pleasure to the further information he had promised to lay before the Society. He, nevertheless, entertained considerable doubt as to the propriety of applying microscopic examination as the sole test for the passing of samples of butter.

#### A NEW AND RAPID METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC BODIES.

BY W. F. KEATING STOCK, F.C.S., F.I.C.

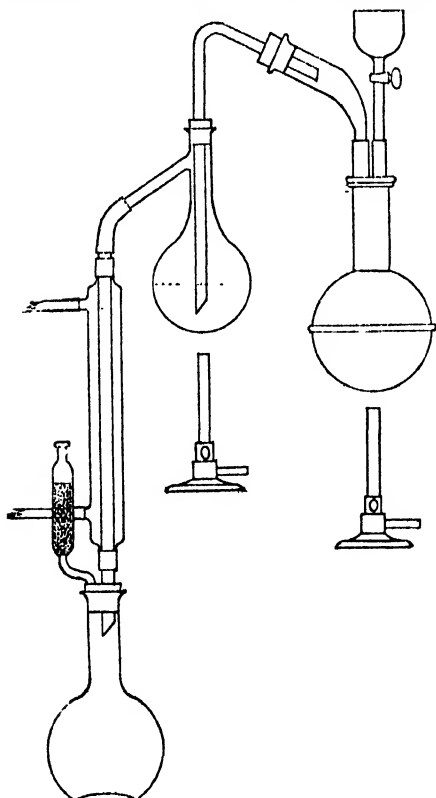
HAVING frequently been struck with the ready reduction of manganese dioxide in even slightly acid solutions, containing organic matter, it occurred to me to ascertain the possibility of turning this re-action to account, in the determination of nitrogen in organic combination.

Preliminary experiments proved that such substances as bones, cotton seed cake, linseed cake, fish flesh, pepper, and even coal and hard Durham coke, could be perfectly and rapidly oxidised by treatment with strong sulphuric acid and finely powdered manganese ore, at a temperature much below the boiling point of the acid.

It was also proved that the nitrogen of these bodies was thus converted into ammonia.

After a few trials with a "one to one" mixture of sulphuric acid and water, this was abandoned in favour of the strong acid, because it was found that the weaker acid led to a good deal of frothing. Eventually the process assumed a workable aspect, and stands as follows:—

From 0.5 to 1 gram of substance, according to the carbonaceous matter to be oxidised, is mixed in a conical flask or small beaker with 10 c.c. sulphuric acid of 1.84 specific gravity, and 5 grams of native manganese dioxide, which has been made to pass through a sieve with 36 holes to the linear inch. It is important that the oxide shall be fine enough, and yet not too fine. The flask is heated on an iron plate, until the contents assume a dark green colour, owing to the formation of manganic sulphate. This indicates the end of the re-action. The flask is cooled, cold water is added, and the contents transferred to an apparatus presently to be described. An excess of sodium hydrate in solution (20 grams for 10 c.c. sulphuric acid) is added, and the ammonia is distilled, collected, and titrated in the usual way.



The apparatus, which is shown in the accompanying figure, consists of a copper boiler of 600 c.c. capacity, closed by a screw cap and india-rubber washer. This cap carries a tapped funnel for the introduction of the sodium-hydrate solution, and a wide evolution tube to serve as a reflux tube, in case of sudden frothing. The evolution tube is closed by an I.R. stopper, carrying a tube bent at such an angle as will permit its passing down the centre of a Wurtz flask, which serves as a washing flask for the vapours from the copper boiler. Both boiler and flask are provided with burners, and both must be kept boiling throughout the experiment. The Wurtz flask is in turn connected with a 14-inch Liebig's condenser, set vertically, and this terminates in a 500 c.c. receiving flask, fitted with a guard tube filled with beads, through which the standard acid is run into the receiver. The open-ends of the tubes are all ground off at an acute angle, so as to prevent the formation of piston-drops.

Some remarks on the apparatus may not be out of place. I have adopted a copper boiler because, even when using the best bolt-heads I could procure, the fractures amounted to about 25 per cent., although zinc was used to lessen the bumping. With the copper boiler zinc is quite unnecessary, the boiling goes on in perfect quiet, and, so far as I see,

the copper flask does not suffer. The Wurtz flask, cannot, in my opinion, be dispensed with. I have tried every plan that would occur to an old campaigner to keep the sodium-hydrate back, but, without this intermediate flask, I have failed to get results to my satisfaction.

The method now disclosed cannot be looked upon as simply a modification of Kjeldahl's process. Kjeldahl effects oxidation at the expense of sulphuric acid; and although he uses potassium permanganate, to complete the oxidation, he does not rely upon it as a principal re-agent.

Kjeldahl's method requires much more time than the method I propose. I have completely oxidised a sample of bone powder in three minutes, and have determined the nitrogen in fifty minutes from the time of weighing out the sample.

I am making quantitative trials of the method as opportunity offers; new methods always require a little practice—I have compared it with the soda-lime combustion process on several samples of bone-dust, and the results from the two processes, whilst agreeing excellently among themselves, differ very little from each other.

The following will show what has been attained in the way of agreement:—

|             | Nitrogen by Combustion. |                | Nitrogen by New Method. |                |
|-------------|-------------------------|----------------|-------------------------|----------------|
| Bone meal   | ...                     | 3.54 per cent. | ...                     | 3.64 per cent. |
| Cotton cake | ...                     | 3.69 „         | ...                     | 3.49 „         |
| Fish flesh  | ...                     | 7.41 „         | ...                     | 7.51 „         |

It may be well to add a word of caution as to a source of loss of ammonia. Manures or other matters, containing a notable proportion of chlorides, could not be treated at once by this method. The chlorides must be decomposed by heating with sulphuric acid alone for twenty minutes, and the manganese dioxide can then be added at once, and this leads me to add that I have found a finely divided manganese dioxide, which has been given to me by my friend, Mr. John Pattinson, of Newcastle, as being a pure oxide, obtained by a "recovery process" on the large scale, to supply the place of Kjeldahl's permanganate, as used in his process, admirably, and to give infinitely less trouble.

It will occur to chemists that, in using this method, a "blank" experiment must be made with the re-agents, just as in Kjeldahl's process.

The following are further experimental results obtained by this method:—

| FISH FLESH.              |                          |  |
|--------------------------|--------------------------|--|
| By New Method.           | By Combustion.           |  |
| 7.45 per cent. Nitrogen. | 7.41 per cent. Nitrogen. |  |
| 7.45 „ „                 |                          |  |
| 7.47 „ „                 |                          |  |
| 7.51 „ „                 |                          |  |
| 7.45 „ „                 |                          |  |
| COTTON SEED CAKE.        |                          |  |
| By New Method.           | By Combustion.           |  |
| 3.61 per cent. Nitrogen. | 3.68 per cent. Nitrogen. |  |
| 3.49 „ „                 |                          |  |

## COMMERCIAL URIC ACID.

(Containing 99.3 per cent of uric acid)

| Found.                    | Theoretically. |
|---------------------------|----------------|
| 32.70 per cent. Nitrogen. | 33.09          |
| 32.51       "       "     |                |

## COMMERCIAL GELATIN (NELSON'S).

Two determinations gave 14.61 and 14.27 per cent. Nitrogen.

None of these determinations occupied more than one hour. Beakers of 180 c.c. capacity were used *for the oxidation*.

Attempts have been made to use the method for determining the nitrogen of ferrocyanides and some alkaloids, but so far without success.

## DISCUSSION.

The President believed that the members of the Society would agree with him in thinking that any process which tended to simplify the determination of nitrogen—if experience showed that such method was so generally applicable as the Kjeldahl process was acknowledged to be—would be a valuable one to analysts.

Mr. Bernard Dyer wished, without criticising Mr. Stock's process, which he had not yet had an opportunity of trying, to take the opportunity of saying through the medium of *THE ANALYST*, that the use of permanganate in the Kjeldahl process—mentioned by Mr. Stock—was a decided mistake. It was not only quite unnecessary, but, in some cases, it might be a very serious source of error. Mr. Coste, and he, had made a number of experiments with the Kjeldahl process, with a view to testing the effect of the permanganate, and they had found that the use of it was very liable to occasion a loss of nitrogen. It was quite unnecessary, in the Kjeldahl process, to use permanganate at all. The best form of the Kjeldahl process was that in which sulphate of potash was used to raise the boiling point of the acid, and a drop of mercury added. In the figures which Mr. Stock had given, the use of manganese di-oxide did not appear to have produced any disastrous results; but he should advise anyone, before relying on it, to make experiments under various conditions, notably with known quantities of pure ammonia salts, bearing in mind the peculiar effect of permanganate in the kindred Kjeldahl process.

Mr. F. H. Perry Coste strongly endorsed Mr. Dyer's fears as to the danger of using manganese di-oxide. He considered that Mr. Stock had not proved his case, in spite of the closeness of the agreement between the results of the two processes. It would have been more satisfactory if he had made the check experiments by the usual Kjeldahl process. He wished also to point out that Mr. Stock had given very little information as to experiments with pure salts. In the only instance quoted (uric acid) the agreement was by no means close. Mr. Stock further stated that he entirely failed with ferrocyanide. This seemed to him a very important admission, seeing that the total nitrogen of ferrocyanide was readily obtainable by the Kjeldahl process.

Dr. Samuel Rideal pointed out that the addition of manganese di-oxide to the

sulphuric acid no doubt raised the boiling point, just in the same way as the addition of potassium sulphate did in the Kjeldahl process as worked by Mr. Dyer.

Mr. Coste stated that, by the use of potassium sulphate and mercury, one could complete the digestion in three-quarters of an hour, that being sufficient time for even such substances as gelatin.

Mr. Dyer explained that the essential difference between the two processes was that Mr. Stock did not boil, and so did not effect the oxidation at the expense of the acid.

Mr. Richmond's papers were deferred to the next meeting.

The Society's proceedings then terminated.

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### ON A RECENT CASE OF BUTTER ADULTERATION.

By CHARLES E. CASSAL.

*Read at Meeting, April, 1892.*

THE unsatisfactory state of things which may result under the present system of referring disputed cases of adulteration to Somerset House has been called attention to again and again. I greatly regret that it should fall to my lot to place one more instance on the long record of cases of difference between Public Analysts and the Chemists at Somerset House, for, were it possible, I think that it would be far preferable to deal with matters in dispute between us and those who are, after all, our professional colleagues, by methods other than those involved in public controversy. But I have no option in the matter; there is at present no other practical course open, and I hold that it would be wrong for a Public Analyst to submit tamely to the dismissal of cases undertaken on his certificates, because a Government Department sees fit to adopt singular and indeed *outré* views, and lest he should be taken as acquiescing in the maintenance of a system which is fundamentally bad, and which, in consequence, has often worked to the detriment of the analytical profession and to the injury of the public service.

In the month of December of last year a sample of butter was brought to me for analysis by an Inspector under the Acts. It had been purchased in a country district, within a short distance of the East coast. I certified that it contained at least 15 per cent. of foreign fat. I sent a portion of my sample to our President, Mr. Hehner, who certified it to contain 16 per cent. of foreign fat. The case was disputed, and the Inspector's reserve sample was sent to Somerset House. The certificate drawn up by the Chemists there, contained, as usual, and, as I hold, very improperly, statements of the percentages of water, "curd," salt, and fat—analytical details of no real bearing on the point at issue—and went on to state that "the result of a full analysis of the fat shows that the butter practically falls within the limits of the poorest quality of genuine butter met with in commerce, and they do not, in our opinion, afford evidence that foreign fat has been added to the butter."

With reference to the statements of the percentages of water, curd, salt, and fat, I may refer to a paper which I read at the February meeting of the Society, on "The

Drawing up of Certificates," in which the practice of the Somerset House Chemists in this respect was alluded to. I pointed out that these data have no bearing on the points at issue, and that their appearance in the certificates casts an unjustifiable reflection on the Public Analyst, implying, as it does, that these data should also appear in the certificate issued by him. The data relating to the analysis of the fat do not, however, appear in the Somerset House certificates.

I think that the Society will appreciate the reasons why I avoid mentioning analytical details in this case. I place the whole matter on this basis—that two Public Analysts, one of them the President of the Society of Public Analysts, and in addition to that fact, also one of the best known, if not the best known authority on the analysis of butter, have certified that a sample of butter was adulterated, practically to the same extent; and in view of the remarks I made on a previous occasion as to the undesirability in such cases as the present, of advertising analytical data, I do not think it well to publish them; but I will, of course, state them to the Society.

It will be observed that the wording of the Somerset House certificate is in some respects exceedingly cautious; but what it is that constitutes "poorness" of butter-fat is a question immediately raised by it. The term is inapplicable. It must, however, be held to mean that the fat departed to some extent in character from butter-fat, in the view of the Somerset House Chemists; and it plainly implies inferiority. From an analytical point of view, the fat of butter, or any fat, as such, can only justly be regarded as inferior in consequence of a difference in composition from that normally appertaining to the fat in question, such as would result from the presence of another fat; that is, *analytically*, inferiority of the *fat* of butter, if admitted, can only be constituted by the presence of another fat. I say, advisedly, inferiority of the *fat*. A butter may be poor; but I contend that in the present state of our knowledge it is not competent for anyone to talk of a "*poor*" butter-fat, except in the sense which I have indicated. A theory on this matter has been tentatively suggested to me; namely, that "poorness" in volatile fatty acids might constitute a "*poor*" butter-fat. If this were adopted as characterising a "*poor*" butter-fat, and if a butter-fat whose volatile fatty acids fall below a certain percentage is inferior in quality, then we have a possible definition; but until such a definition is made, and generally accepted, there is no such thing as "*poor*" butter-fat. It might properly be held that by the sale of a butter which was poor in volatile acids, and rich in fixed fatty acids, a purchaser was in no way injured, and that the butter was not in any sense inferior. It might even be looked upon as superior.

To Public Analysts the meaning of the Somerset House certificate is sufficiently obvious. I need hardly point out that it is on all accounts to be regretted that the Chemists who drew it up should differ from the great majority of Public Analysts in adopting indefensibly wide limits, and in showing so much leniency. The occurrence of cases of this kind is the more unfortunate as Somerset House is often erroneously looked upon as a sort of Court of Appeal. Some Magistrates have a habit, and a very bad habit it is, of taking the *dictum* of Somerset House as final. But it should be



pointed out that Magistrates are not only not compelled to adopt that *dictum*, but that it is undesirable that they should do so. They are bound only by the weight of the evidence that is before them. It would not be really difficult to show that the *dictum* to be relied on is that of the Council of the Society of Public Analysts, and not that of Somerset House. All matters of this sort should, in my opinion, be regulated by the Council of the Society of Public Analysts.

Somerset House may be regarded as a sort of Court for confirmation, which has again and again been proved to be quite mistaken; and once again in the present instance, for there is no reason to believe that there was any material difference between the Inspector's reserve sample and that analysed by Mr. Hehner and myself. The Court for confirmation, if it be one, is not to be looked upon as being abnormally free from the errors that beset mankind because it is a Government department, or on the strength of any other shibboleth. The Somerset House analysts are not necessarily more correct in their views and more certain in their results than any other analysts; I am, indeed, convinced that in their private capacities they would be the last persons to arrogate to themselves any such monopoly of knowledge and of accuracy. They have, at any rate, the distinction of being in an almost infinitesimal minority: but the fact remains that the Public Authorities concerned with the suppression of adulteration and the Public Analysts appointed by them are placed in a position of much difficulty in consequence of their undoubtedly conscientious, but mistaken action.

A discussion ensued in which the President, Dr. Alfred Hill, Dr. Vieth and others took part, and Mr. Cassal replied.

**Volumetric Estimation of Sulphuric Acid in Sulphates. E. Stolle.** (*Zeitsch. f. angew. Chem.* 1892, p. 234.)—Precht has modified Wildenstein's method by adding standard chromate in excess and titrating back the excess by means of a ferrous solution. The author further modifies the method by using a solution of barium chromate in the following manner:—A solution of barium chloride is precipitated hot with a slight excess of potassium chromate, a little barium chloride being finally added till the fluid is colourless. The precipitate is washed with hot water and is then dissolved in dilute hydrochloric acid.

The sulphate to be analysed is precipitated with a slight excess of this solution, ammonia is added, whereby the whole of the sulphuric acid is precipitated as sulphate, whilst a quantity of chromic acid, equivalent to the sulphuric acid which was present, is liberated and remains in the solution. This is filtered, and the chromic acid in the whole filtrate, or an aliquot portion of it, after acidification, is titrated with a standard ferrous solution. The results are very satisfactory and speedily obtained. Only one standard solution, that of the ferrous salt, is required. The author recommends an hydrochloric barium chromate solution of about 1.06 spec. gravity.

O. H.

**On the determination of Phosphoric Anhydride in Thomas Slag.** (*Staz Sper. Agr. Ital.* xix., 614 ; xx., 159 ; xxi. 225 and 453.)

The processes for attacking the slag are as follows :—

- (1) With hydrochloric acid and potassium chlorate (three times the weight of the slag). (Olivieri.)
- (2) With sulphuric acid (5 c.c. for each gram.), heating over naked flame until white fumes escape. (Loges.)
- (3) With hydrochloric acid, 15 c.c. for each gram. of slag, evaporating to dryness to separate silica. (Konig-Martelli.)
- (4) With aqua regia.

The solution is made up to a known bulk, and a quantity containing '1 — '2 grs.  $P_2O_5$  is taken, 20 c.c. of a citric acid solution is added, and the solution nearly neutralized with 10 per cent. ammonia. After cooling 25 c.c. of magnesia mixture is added (a much larger quantity in the presence of much manganese. *Stutzer Land. Versuchs.*, 1890, 291), the mixture shaken till a precipitate begins to form, and  $\frac{1}{2}$  of its bulk of 10 per cent. ammonia added. The precipitate is collected in the usual way and weighed as  $Mg_2P_2O_7$  (Martelli, c. f. Konig, Martinotti and Olivieri.)

Mancusa-Limo adds to 2 grs. slag 25 c.c. dilute sulphuric acid (1 : 1), stirring well, and after two hours' repose adds warm water, filters and neutralizes with milk of lime ; the liquid containing the precipitate, which darkens on exposure to the air, is heated on the water bath for half an hour, and then nitric acid is added till the precipitate is dissolved ; the solution is cooled and filtered from silica, &c. The phosphoric acid is precipitated with molybdate, and converted into magnesium pyro-phosphate in the usual way.

The citrate method is inclined to give slightly high results, and the molybdate slightly low ; with much manganese the latter is preferable.

H. D. R.

**A Volumetric Method for the Estimation of Phosphoric Acid.** By Matteo Spico. (*Gaz. Chim. Italiana*, xxii., i. 117.)—The author takes advantage of the fact that a solution of a phosphate added to a ferric solution produces a precipitate of ferric phosphate  $FePO_4$ , and the precipitation is complete, provided that complete neutrality is secured.

After obtaining his phosphate in solution (iron, aluminium, and manganese salts must be absent), he neutralises exactly with caustic alkali, using phenolphthalein as indicator ; he then adds a small quantity of salicylic acid, and titrates with a solution of ferric ammonium alum (1 c.c. = '001 grm.  $P_2O_5$  previously standardised on a solution containing containing 2.9439 grm. microcosmic salt per litre of which 1 c.c. also = '001 grm.  $P_2O_5$ ), adding it in small quantities at a time, especially during the latter part of the titration ; it is desirable to wait a little to let the white precipitated ferric phosphate settle down somewhat, as then the violet colour produced by the least excess of ferric solution is more easily seen.

The test experiments made with theoretical mixtures, minerals, and Thomas slag are very satisfactory, and the method agrees well with those of Olivieri, Mancuso, and Martinotti. (Compare preceding Abstract.)  
H. D. R.

**Observations on Butter Analysis.** F. Jean. (*Revue Inter. d. Falsifications*, 1891, 65.)—A sample of pure butter forwarded by the Dutch chemists, Lobry de Bruyn and Van Leent, gave a R-W. figure of 20.75 and deviated to the left 20° of the author's oleo-refractometer.

The author suspected that the cow had been fed with linseed cake, which, according to Kildan's theory, should lower the soluble fatty acids; this theory is confirmed by Girard, who fed a cow with 2 kilo of linseed cake a day for 8 days, and then found 23.6 c.c. R-W. figure and—20° deviation in the oleo-refractometer. On increasing the amount of linseed cake to 4 kilos after 15 days he found 21.6 c.c. and — 17° respectively.

He shows that high refracting adulterants (*e.g.*, linseed oil), affect the oleo-refractometer reading much more than they do the Reichert-Wollny figure; thus a butter with a vegetable adulterant in small quantity gave 27.9 c.c. R-W. and — 23° deviation, while with an animal fat he obtained 26.4 c.c. R-W. and — 29° deviation.

The oleo-refractometer cannot decide in all cases whether a butter is genuine or adulterated, but it can be used to sort out samples as genuine, doubtful, and adulterated.

When a cow is fed on linseed cake (or, indeed, any other oil cake), the foreign fat passes into the butter.

Replying to the above, De Bruyn and Van Leent (*Revue Inter. d. Falsifications*, 1891, 78), admit the influence of linseed cake on the butters; it is largely used in Holland in the winter as an addition to hay. Their published analyses show that it has a much greater influence on the refractive index than on the volatile acids. They dispute the usefulness claimed by Jean for his oleo-refractometer even for sorting butters, because pure Dutch butters gave such discordant results.

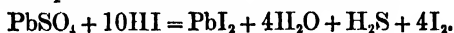
H. D. R.

**On the Analysis of Galena and Lead Sulphate.** R. Benedikt. (*Chem. Zeit.* 1892., xvi. 43, 44.)—The chief difficulty in the analysis of galena arises from the presence of gangue, from which the lead sulphate produced by the action of strong nitric acid and subsequent evaporation with sulphuric acid, has to be extracted either by repeated treatment with hydrochloric acid or with ammonium tartrate or acetate, or by digestion with sodium carbonate and subsequent solution in dilute nitric acid. The author has previously shown, in conjunction with M. Bamberger (*Monatshefte f. Chemie.*, 1891, xii. 1), that soluble sulphates, especially potassium sulphate, are easily converted into iodides by treatment with hydriodic acid, while barium sulphate is attacked more slowly. Free sulphuric acid is reduced to sulphuretted hydrogen. The method of analysis based on these facts is as follows: the sample is powdered finely enough to allow of a represen-

tative portion being taken, and a weighed quantity treated with a few c.c. of hydriodic acid of specific gravity 1.7, in a hemispherical porcelain dish. In order to avoid a too violent action it is best to cover the portion taken with a little water before adding the acid. After digesting for a short time on the water bath the contents of the basin is taken to dryness, allowed to cool, treated with dilute nitric acid, and again warmed, the lead being thus converted into nitrate, with separation of iodine.

The iodine is driven off by evaporation, the residue moistened with dilute nitric acid, the solution filtered, and the lead estimated in the filtrate by treatment with sulphuric acid in the usual way. A second digestion with hydriodic acid may be performed, but is rarely necessary. Test analyses, both on approximately pure lead sulphide, and on galena containing a good deal of gangue, as well as the sulphides of copper, zinc and antimony, gave satisfactory results.

In the case of lead sulphate the reaction is as follows:—



A considerable quantity of iodine is set free, and this, acting on the sulphuretted hydrogen, liberates sulphur, which is deposited on the walls of the beaker. Otherwise the analysis proceeds as described above for galena.

The separation of sulphur may be avoided by covering the original substance before treatment with hydriodic acid, with water in which a small quantity of amorphous phosphorus is suspended, whereby the iodine is reconverted into hydriodic acid. A test analysis gave a satisfactory result. The author considers that the analyses of other sulphides may be facilitated by the use of hydriodic acid, and that the action of dilute nitric acid upon lead iodide may be taken advantage of in separating silver and lead. B. B.

**The Rapid Determination of Free Sulphuric Acid in Aërated Waters.**  
**P. Cazeneuve and Nicolle.** (*J. Pharm. Chim.*, 1892, xxv. 51, through *Chem. Zeit.*).—Aërated waters often contain free sulphuric acid carried over mechanically from the generator. The amount is usually about 0.25 grams per litre, but occasionally is as much as double this. The process recommended by the author for its rapid detection and approximate estimation, depends upon the fact that calcium carbonate is precipitated when aërated waters are added to lime water, and dissolves in excess of the former, being reprecipitated on heating, and that should the aërated water contain a trace of free sulphuric acid this precipitate of calcium carbonate does not form, being converted into calcium sulphate, which remains in solution. The reagent used is lime water saturated at the ordinary temperature and free from any trace of alkali. One litre of water dissolves 1.29 grams of CaO at 15° C., 1 c.c. of the solution, therefore, corresponding to 0.0022 grams of sulphuric acid. 1 c.c. of the lime water is placed in each of five test tubes, and then 4 c.c., 8 c.c., 12 c.c., 16 c.c., and 20 c.c. of the aërated water to be tested added respectively. Should a turbidity appear in all the tubes on heating, the quantity of free sulphuric acid is negligibly small. Should, however, for example, the contents of the

third tube remain clear, while the second becomes turbid, the quantity of sulphuric acid necessary to neutralise 1 c.c. of lime-water is contained in something between 8 and 12 c.c. of the aerated water. The precise volume requisite can then be found by repeating the process with 9, 10 and 11 cc. of the aerated water. An obvious calculation gives the content of sulphuric acid per litre.

B. B.

**The Examination of Wall Paper, Carpets, and Textile Goods for Arsenic, in Sweden.** J. Landin. (*Chem. Zeit.*, 1892, xvi. 420.)—During the period from November, 1884, to the end of 1891, 9,632 analyses for arsenic in various textile materials and in paper hangings were carried out at the Kemiskt-tekniska Byran, in Stockholm, the main results of which are appended. The official method for the detection of arsenic prescribes that the arsenic shall be obtained as sulphide, and reduced by heating with potassium cyanide and sodium carbonate. If, when this is performed in a glass tube 1.5 to 2 mm. in internal diameter, a black or brownish-black mirror which is, at least in places, opaque, be formed, the following goods are condemned: Wall paper, roller blinds, artificial flowers, and similar articles coloured with water colours, when the test gives a positive result upon a quantity equal to 200 sq. cm. or less; all sorts of textile stuffs, yarn, lamp shades, sealing wax, wafers, stearin and other candles, when arsenic can be detected upon 100 sq. cm. or 21 grms., as the case may be. The method of examination is as follows: The article to be tested is distilled in a flask of about 300 c.c. capacity with 50 c.c. of hydrochloric acid of specific gravity 1.18-1.19, and 2 grms. of ferrous sulphate, both free from arsenic. In the case of so-called gold or bronze paint and other metallic articles, 2-3 grms. of ferric chloride are added. The distillate is received in 50 c.c. of water, and treated with 50 c.c. of a saturated solution of sulphuretted hydrogen. The precipitate of arsenious sulphide is collected on a filter 6-7 cm. in diameter, washed, and dissolved in dilute ammonia. The solution is evaporated to dryness after the addition of 0.02 grms. of sodium carbonate, and the residue is then heated in a bulb tube with 0.3 grms. of a mixture of dried sodium carbonate and potassium cyanide, in a stream of carbonic acid. The following are the numbers of the various articles examined:—

|                |     |     |     |     |     |     |       |
|----------------|-----|-----|-----|-----|-----|-----|-------|
| Wall papers    | ... | ... | ... | ... | ... | ... | 3,779 |
| Textile goods  | ... | ... | ... | ... | ... | ... | 3,601 |
| Carpets        | ... | ... | ... | ... | ... | ... | 1,084 |
| Colours        | ... | ... | ... | ... | ... | ... | 305   |
| Plush articles | ... | ... | ... | ... | ... | ... | 227   |
| Yarn           | ... | ... | ... | ... | ... | ... | 220   |
| Thread         | ... | ... | ... | ... | ... | ... | 137   |
| Linoleum       | ... | ... | ... | ... | ... | ... | 106   |
| Miscellaneous  | ... | ... | ... | ... | ... | ... | 173   |

The following table shows the percentage that were found to contain arsenic, and of those the percentage which contained sufficient arsenic to yield an opaque mirror:—

|                              |     |     |     | Containing<br>arsenic. | Percentage of those<br>containing much arsenic |
|------------------------------|-----|-----|-----|------------------------|--|
| Linoleum                     | ... | ... | ... | 59.4                   | 38.1   |
| Carpets                      | ... | ... | ... | 55.3                   | 31.1   |
| Wall papers                  | ... | ... | ... | 55.2                   | 39.1   |
| Plush                        | ..  | ... | ... | 52.3                   | 66.2   |
| Yarn                         | ... | ... | ... | 45.0                   | 44.4   |
| Colours                      | ... | ... | ... | 43.3                   | 74.4   |
| Miscellaneous                | ... | ... | ... | 41.4                   | 75.3   |
| Textiles                     | ..  | ... | ... | 21.2                   | 47.3   |
| Thread                       | ... | ... | ... | 20.4                   | 35.8   |
| Average for the whole number | ... | ... | ... | 41.2                   | 42.2   |

From these figures it appears that of the whole number of articles examined, 17.4 per cent. contained enough arsenic to lead to their condemnation. An improvement appears to be taking place, as the corresponding number for 1891 was 11.3 per cent. Of textile materials, those uniform in colour were freer from arsenic than those variegated in colour. Of brown fabrics 19.1 per cent. contained arsenic, while for other colours the figures were—red, 15.7 per cent.; green, 10.7 per cent.; blue, 10.6 per cent.; yellow, 6.8 per cent.; black, 3.0 per cent. White and grey fabrics were almost always free from arsenic.

B. B.

## CORRESPONDENCE.

THE YEWS, REIGATE,

May, 18th, 1892.

GENTLEMEN,

*To the Editors of THE ANALYST.*

In a communication to the Society of Public Analysts, printed in your issue for the present month, Mr. Leo Taylor finds fault with me because I could not give an opinion as to the hygienic quality of certain samples of water from data furnished by his analysis. These data were "loss on ignition," "oxygen required to oxidise organic and other matter," and "organic ammonia."

I have elsewhere (*Jour. Chem. Soc.*, vol. xxi. p. 77, and vol. xxix. p. 825) stated very fully my reasons for rejecting these processes as indicators of organic impurity. It was only after I found that they condemned unpolluted mountain waters and did not convict impure shallow well waters, that I was compelled to abandon them. I came to this conclusion reluctantly, inasmuch as these processes can be carried out in a few hours, whilst the combustion process occupies several days.

Mr. Leo Taylor's analyses did not, as he alleges, include any estimation of "nitrogen as nitrates and nitrites," and therefore this trustworthy datum was not before me.

In conclusion, there can be no doubt that the rapid methods employed by Mr. Taylor find most favour with the great majority of chemists; but in cases of importance, such as the water supply of towns, recourse is almost always had to the combustion process.

I am, &amp;c.,

E. FRANKLAND,

# THE ANALYST.

JULY, 1892.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The usual Monthly Meeting of the Society was held on Wednesday, 1st June, the President (Mr. Hehner) occupying the chair.

The minutes of the last meeting were read and confirmed.

The following gentlemen were proposed as members:—A. P. Aitken, D.Sc., Chemist to the Highland and Agricultural Society of Scotland, 8, Clyde Street, Edinburgh; Frederick Wm. Tompson, F.C.S., Chemist in the employ of Messrs. Bass & Co., Brewers, Burton-on-Trent, Stapenhill Road, Burton-on-Trent; and John Williams, Private Assistant to Professor J. B. Harrison, Government Analytical Chemist, British Guiana, Georgetown, Demerara, was proposed as an associate.

Messrs. Samuel Francis Burford, F.C.S.; James William Westmoreland, F.I.C., were duly elected members of the Society; and Messrs. G. H. Gabb and W. N. Yarrow, were duly elected associates.

Mr. H. Droop Richmond read the following "Notes from the Khedivial Laboratory, Cairo":—(7) "On a Sample of Milk yielded by an Arab Woman." (8) "Egyptian Flour." (9) "Some Egyptian Waters." (10) "The Manganese beds of Assiout." The publication of these papers is unavoidably held over until next month.

In the absence of Dr. Leather, Mr. Dyer read the following paper:—

### THE DETECTION OF CASTOR OIL SEED AND OF CROTON SEED IN FEEDING STUFFS.

By J. WALTER LEATHER, Ph.D., F.I.C.

As is well known, both castor oil seed (*Ricinus communis*) and the seeds of croton (*Croton tiglium*) are very poisonous.

A small admixture, even considerably less than one per cent., of either of these seeds, when present in a cattle food, is sufficient to cause harm and even death. An ordinary

search with the microscope for any seed existing in smaller proportion than one per cent. would, in any case, be not only very tedious, but might fail to detect the constituent.

The difficulties attending a microscopical search for either of these seeds are, however, considerably increased on account of the "seed case" of each being quite impervious to light, and the structure being, in consequence, indiscernable.

The method which I have employed for some time past for the microscopical examination of foods, so far as the recognition of the testa of seeds is concerned, is, firstly, to digest a portion of the material with dilute  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  (1 to 2 per cent.) for half-an-hour on the water-bath; then to remove the acid liquid by decantation and to wash the material several times in the same manner; secondly, to digest it with equally dilute  $\text{KHO}$  or  $\text{NaHO}$  and to repeat the washing by decantation. In this way I have found that the testæ of all those seeds which one generally meets with in cattle foods, and also the impurities which frequently accompany them, are rendered sufficiently transparent to be readily recognized under the microscope. After washing the alkaline liquid away, it is sometimes an advantage to wash the material with dilute  $\text{HCl}$ , which reduces the strong colour produced by the action of the alkali. I do not lay any claim to this process, for I believe that many chemists employ both acid and alkali for the above purpose, but I might mention that I have not met in text-books with any directions for their use in the manner I have indicated.

Now, if either castor oil seed or croton seed be subjected to this process, the outer integument of each is washed away, and the principal part of the testa remains black and opaque. At the edges some indication of the structure can frequently be seen.

In any case, owing, as I have said, to the fact that it requires but a very small quantity of either of these seeds, probably 3 or 4 seeds, or less, per lb., to cause serious illness or death to stock, the examination with the microscope of one or two grammes of a material could not be expected to expose their presence with certainty.

During a search, some months ago, for these seeds in some decorticated cotton cake, I subjected a number of pieces which had been picked out with the aid of a pocket lens, to the action of a solution of sodium hypochlorite. I had previously employed this agent to bleach similar materials for another purpose, and I had always found that it removed the colour entirely after a few hours. I therefore hoped that I should in this way obtain a view of the structure of castor oil seed and of the pieces above referred to. To my surprise, however, they remained perfectly unbleached, even at the end of several days. I then subjected a number of pieces of the testæ of both castor oil seed and croton seed (1) to the action of dilute acid and alkali and (2) to sodium hypochlorite. The result was that the seeds remained entirely unbleached. At the same time I treated in the same manner the testæ of cotton seed, *Bassia*, *Polygonum convolvulus*, and locust-bean, all of which, especially the first-named, are very dark-coloured. In every case they bleached quite readily. Free chlorine has a more energetic action, and will gradually bleach both



castor oil seed and croton seed ; the time required amounted, however, in my experiments to some three or four days, and even then the colour was not completely discharged. I need not mention other seeds, which are likewise dark-coloured, and which frequently occur in cattle foods, for they present no difficulty in their recognition. I had now in my hands a method by which either castor oil seed or croton seed might be readily separated from other materials, even when present in quite small quantity. If the suspected feeding stuff be first digested with acid and alkali, and be then subjected for a few hours to the action of bleaching powder, any castor oil seed or croton seed would remain black amongst the bleached mass. I may mention here that preliminary experiments had shown me that this agent acted exactly in the same manner as sodium hypochlorite. In order to put the method to a test, I chose undecorticated cotton cake as the material with which to mix the castor oil seed or croton seed. I made this selection because the testa of the cotton seed is just as black after treatment with acid and alkali, as that of either castor or croton.

To one pound of the coarsely ground cotton cake I added, in each of the following experiments, the weighed and coarsely broken up testa of *one seed* of castor and croton respectively, and, after mixing roughly, the whole was digested in dilute HCl and boiled for one hour by passing a current of steam through it. After washing by decantation, the mass was boiled with dilute alkali for a similar period, and again washed by decantation until the washing water was colourless. Bleaching powder, about  $\frac{1}{2}$  lb. to 1 lb. (the exact quantity does not appear to be material) was then added, and sufficient water to keep the temperature from rising. This was usually three or four litres. The mass was stirred occasionally and left over night, although the bleaching action was frequently complete at the end of four hours. Washing by decantation now followed, by which means most of the lime could be removed. It remained now merely to pick over, by hand, the bleached material and select the unbleached pieces for examination. This operation requires, for a pound of material, some considerable time, varying from one half to a whole day, but it is so simple that any careful laboratory servant can perform it. Care must be taken not to have anything thrown away. The picking over of the material is most readily performed by spreading small quantities on the bottom of a flat porcelain dish, which is about half full of water ; any dark-coloured or black pieces can then be easily seen, and can be taken out. After the unbleached pieces have been separated they are readily examined, and anything other than castor or croton again separated. I may mention here that in a pound of bleaching powder a number of bits of coal or stone may often be found, and, further, in the case of the cotton seed, the hilum does not always bleach so readily as the other portions, so that these would likewise be separated with any castor or croton seed.

#### EXPERIMENTS—

(1.) Weight of testa of *castor oil seed*, 0.223 grm., mixed with 1 lb. of cotton cake : weight of separated castor oil seed testa, 0.200 grm.

(2.) *Castor oil seed testa*, 0.122 grm., mixed with 1lb. of cotton cake : recovered 0.087 grm. castor oil seed testa.

(3.) *Castor oil seed testa*, 0.065 grm., mixed with 1lb. of cotton cake : recovered 0.042 grm.

(4.) *Croton seed testa*, weight 0.074 grm., mixed with 1lb. of cotton cake : recovered 0.060 grm.

(5.) *Croton seed testa*, weight 0.080 grm : recovered 0.078 grm.

The method, accordingly, is not merely a qualitative one, but is, at the same time, a valuable quantitative one.

Only in one experiment did I fail to recover the greater part of the seed *testa* which was put into the cotton seed cake. In this case 0.071 grm. of the *testa* of croton seed was added, and only 0.02 grm. was recovered. An explanation is, however, easily found for this loss. In a preliminary bleaching experiment with castor oil bean, part of a *mouldy* seed was subjected to the action of sodium hypochlorite, and about one-half of the piece became bleached after the lapse of a day. A microscopical examination revealed, however, the fact that this seed-case had been penetrated through and through with a fungus.

In the experiment in question, the croton seed happened to be a mouldy one, and no doubt a part of it became bleached. With regard to the amount of the seeds which were not recovered in the other quantitative experiments, I believe that the loss was due to very minute pieces of the *testa* being broken off during the process of boiling, the *testa* in each case being extremely brittle, and these minute fragments might naturally be overlooked. Usually, I found that the *testa* of the seed had been broken into some 25 or 30 pieces, by rough pounding with a pestle.

Regarding the hilum of the cotton seed, referred to before as not being completely bleached, there is no difficulty in distinguishing it, for the pieces are round and have no sharp edges ; moreover, they are marked by a series of rings alternating grey and black on the surface.

It now remains for me to speak of the peculiarities of the *testa* of these two poisonous seeds. The outer covering of each is quite distinct, and, in the case of castor seed, very peculiar. If any pieces of either the one or the other seed be found intact no difficulty will be experienced in recognising them. The outer integuments are, however, extremely thin and brittle, and it must not be expected that they will necessarily be present. Of the two, I have as yet only found castor oil seed in any sample of feeding material, and I therefore cannot give any experience as to the other. In the case of castor oil seed, it may very readily happen that this characteristic integument has disappeared, and as a matter of fact I have often found it to be so.

But in the event of no pieces of either of these seeds being found intact, and if they should have been separated by the bleaching process, they are simply black and opaque and extremely similar. One of their chief characteristics is their extraordinary brittle-

ness, and if one endeavours to cut the testa across with the knife, the two parts fly away some considerable distance, and the broken pieces of either have invariably sharp and frequently ragged edges.

Regarding their thickness, I have measured a number of pieces, and find that of the castor oil seed testa to be from 0.25 m.m. to 0.30 m.m., and that of the croton seed testa to be from 0.20 m.m. to 0.25 m.m.; the latter being thus distinctly thinner than the former.

After passing through the bleaching process, the castor oil seed testa has a much smoother and more shiny exterior than the croton seed, and herein lies one point of distinction.

I have examined the microscopical appearance of sections taken transversely through the testa of each. For the greater part, the structure of each is very similar, each being built up of closely packed bundles of fibres of the same thickness. One difference I have noticed is, that on the outermost edge of the section of the croton testa there is a distinct thickening of each bundle of fibres, whereas this is quite absent from the section of the castor oil seed testa.

Lastly, if the edges of the pieces be examined with a low power objective (about 1 in.) with reflected light, the peculiar curvature of the bundles of fibres on the inner edge is readily seen. This is common to both of the seeds.

#### DISCUSSION.

Mr. Bernard Dyer said that castor seed found in feeding stuffs was sometimes in the decorticated form. One small piece of husk might then represent a large amount of castor seed.

The President asked Mr. Dyer if this impurity was accidental, or was the seed added intentionally?

Mr. Dyer replied that he was of opinion that sometimes it was added accidentally and sometimes intentionally. In a good many cases it had been found in Brazilian cotton meal and cake; and in that case he believed the castor oil seed had been accidentally introduced, through the castor oil plant growing as a weed among the cotton; but in some cases he was sure that it was deliberately added through ignorance. There was an enormous quantity of castor cake produced, especially in tropical countries, which ought all to be used as manure. It was sometimes bought up by people who were ignorant of its poisonous properties. He had recently had a sample of Niger seed cake sent to him for the purpose of examination, with the view of ascertaining whether it contained castor; and he found that it did. Since then he had found a little castor seed in a sample of linseed cake. He also found a considerable quantity of Niger cake in it, with which the linseed cake had been adulterated, and it seemed not at all improbable that the Niger cake had contained the castor.

Mr. F. H. Perry Coste pointed out with regard to the question that Dr. Leather had referred to at the beginning of his paper—the difficulty of rendering some of those objects transparent—that some microscopical journals had recently given an account of a new process, just discovered, for effecting that purpose. The process was to place the leaf or other object in a drop of glycerin on a slide, cover with a cover-glass, and gently heat, replacing the glycerin from time to time. That method rendered a thick object so transparent that the whole structure of it could be seen. It was, of course, quite different in character from the bleaching process, the colour not being entirely removed. The secret of the process is “the use of glycerin and the saturation of the cells.”\*

Mr. Bertram Blount wished to ask Mr. Dyer if he could inform him whether any attempt had been made to detect castor oil seed by chemical means? He supposed both it and croton seed would be susceptible of detection by recognising the poisonous principles they contained. He believed it was a fact that a poisonous principle had been definitely recognised in castor. As Mr. Dyer had said, there might be only a small quantity of the husk to a comparatively large quantity of the seed, and thus any method of detection, based on the recognition of the husk, was necessarily imperfect.

Mr. Dyer said that he did not think that the definite poisonous principle of castor had been isolated. Professor Tuson, years ago, isolated an alkaloid, which was described in Watt's *Dictionary of Chemistry*, but if he (Mr. Dyer) recollected rightly, that alkaloid did not appear to have been the active ingredient of the seed.

Sir Charles Cameron said that he had some experience in the examination of oil cakes, and on one or two occasions he detected what he believed to be the impurity referred to by Mr. Dyer. He would say, however, that he did not feel great confidence in the results he had arrived at.

Mr. Cassal asked whether it had been attempted to make use of chlorate of potash and hydrochloric acid in the bleaching process described? Mr. Dyer had stated that it took a very considerable time to carry out the bleaching with hypochlorite. He (Mr. Cassal) had found the chlorate of potash and hydrochloric acid method very rapid for vegetable tissue generally.

Sir Charles Cameron said that on one occasion he extracted, by purely chemical treatment, a substance such as that referred to from croton seed, which had strong blistering properties. Its ether extract had acted as a vesicant upon his wrist. It was believed that the cake, in that case, had been very injurious to animals.

Mr. Dyer, replying to Mr. Cassal, said he had not tried the chlorate of potash and hydrochloric acid method. He would expect that method to bleach almost anything. The process Dr. Leather had described was not at all tedious. It was necessary to get rid of the mealy, farinaceous or albuminous part of the meal. That was easily done in an hour or so by the alkali and acid treatment. If the bleaching were

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\*See “Microscope,” xi. (1891), pp. 265-7; and Royal Microscopical Society's Journal, 1892, pp. 287-8.

set going at night, the sample was always ready the next morning. He believed it would be advantageous to use a solution of sodium hypochlorite, which would be free from many of the impurities which were indicated in the paper likely to be present in ordinary bleaching powder. Dr. Leather found that sodium hypochlorite would act in every respect as well as bleaching powder. He thought that the point mentioned by Dr. Leather, with reference to the hilum of the cotton seed, should be carefully noted. The part of the cotton-seed husk which included the hilum did not bleach as a rule, and at first sight looked a little like "unskinned" castor husk; but it was always soft and fleshy at the edges, and if looked at with a low-power magnifying glass, bore no resemblance to castor husk. The latter, when magnified, looked very like a much-diminished fragment of smooth cocoa-nut shell.

Sir Charles Cameron asked Mr. Dyer what he had found certain small particles in decorticated cotton-cake to consist of? The particles in question were very hard and brittle.

Mr. Dyer replied that, if the particles occurred in Brazilian cotton-cake, they were most likely castor.

This terminated the proceedings of the Society.

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## ESTIMATION OF FAT IN MILK BY THE BABCOCK METHOD.

BY ALFRED W. STOKES.

*Read at Meeting, May 4th, 1892.*

In the year 1889, Dr. Babcock, of the United States, introduced a method of determining fat in milk, which could be used by dairymen, and which was rather largely used by the dairymen of the United States and Canada.

This method is now being, to some extent, taken up in England.

About a year-and-a-half ago, Mr. G. H. Clafin, of the Franklin County Creamery, Vermont, kindly gave me his experiences of the method, and spoke very highly of it as a dairy process.

Having lately had an opportunity, through the kindness of Messrs. Welford and Sons, of testing the apparatus, I lay my conclusions before this Society. The essential features are:—A special bottle, one-and-a-quarter inches diameter, and 3 inches high, having a neck, 4 inches long, and  $\frac{3}{16}$  inch diameter. This neck is divided into ten parts, these being subdivided into fifths. The whole bottle holds 50 c.c., of which the neck contains about 2 c.c. Into the bottle 17.6 c.c. of the milk is pipetted, and then an equal bulk of strong  $\text{H}_2\text{SO}_4$  is added. The two liquids are mixed together by gentle shaking. Great heat is developed, the mixture turning quite black. While still hot, the bottle is put into a whirling apparatus, in which four or more bottles can be whirled round at the same time. This centrifugal apparatus is very simple, consisting of a large driving wheel,

15 inches diameter, on a horizontal axis, and having a wide, flat side rim, against which a small india-rubber-tired wheel presses tangentially. This latter wheel is part of the vertical spindle that bears the four arms, on which are cups to receive the bottles. The big wheel has a handle, by which it may be turned, one revolution giving  $6\frac{1}{2}$  revolutions of the little wheel. There is no gearing, friction being all that is necessary. Though looking slight and inefficient, it works very freely and well.

Having placed the bottle, or bottles, in the whirling apparatus, they are kept revolving for eight minutes, at the rate of from 400 to 500 revolutions per minute. Then the bottles are filled up to the beginning of the neck with hot water, and again whirled, this time for two minutes. More hot water is added to near the top of the neck. After whirling for two minutes longer, the fat, which has risen to the top of the water, is read off. The divisions equal percentages and fifths of percentages of fat. The reading off of the percentage of fat is best done while the bottles are immersed in hot water. Otherwise, the fat is spread over the tube as the cooling mass contracts. The great difficulty is to get an accurate reading of the fat. The fat in the tube is not the usual light yellow butter-fat, but a thick viscid brownish mass, often quite black. If the bottles are left for any length of time, after the whirling is finished, black flocks of altered casein will rise and mix with the fat, making the reading almost impossible. Occasionally this happens, however rapidly the reading is taken. The fat being more viscid than melted butter, rarely forms a good column, with a well-rounded base, and a sharp upper meniscus; so that it is not easy to be sure of the reading to a tenth of a per cent.

In the following list I place some results, obtained on milk samples, in which the fat was very carefully calculated, and frequently also determined by the Schmid or paper-coil process, as compared with the Babcock results:—

| Sample. | Calculated. | Babcock.    |
|---------|-------------|-------------|
| No. 1.  | 4.30        | 3.80 & 3.78 |
| 2.      | 4.11        | 3.80        |
| 3.      | 4.09        | 3.80        |
| 4.      | 3.85        | 3.80        |
| 5.      | 3.21        | 3.00 & 3.10 |
| 6.      | 3.17        | 3.00 & 3.00 |
| 7.      | 3.12        | 2.80        |
| 8.      | 3.05        | 3.00        |
| 9.      | 3.00        | 3.00        |
| 10.     | 2.86        | 2.80        |
| 11.     | 2.26        | 2.10 & 2.00 |
| 12.     | 1.70        | 1.20        |

Here we see differences ranging from 0 to 0.5 per cent., with an average difference of 0.21. It is possible that with longer and more experienced working with the apparatus,

the differences might be somewhat less. Never does the Babcock method give results higher than those by calculation.

In an article on this method by Mr. F. T. Shutt (*Chemical News*, vol. 64, No. 1,649), he likewise does not find it to give results above those of reliable gravimetric processes. His average difference he states to be between one and two-tenths of a per cent.

By the kindness of Mr. J. Hampton, the manager of "The Devizes Dairy and Farmers' Supply Co.," I am enabled to place before you a list of fat determinations, on the same samples, by Mr. Hampton, using the Babcock method, and by myself, using the calculation method. As you will see by this list (not printed here), of 18 milks, the results given by the Babcock method are from .08 to .44 per cent. lower than the calculated results, with an average difference of .19. In no case here does the Babcock process show results as high even as the calculated fat.

Looking at one of the bottles after the process is finished, one notices at the bottom a small white sediment; above this is a black liquid, in which floats a quantity of black caseous material; above this, in the neck, is a quantity of water, surmounted by a brown or black viscid column of fat. Examining, microscopically, the white sediment, it is found to consist of a mass of crystals, mixed with a larger quantity of fat globules. It is clear that all the fat does not rise through the dense mixture of acid and milk. More or less fat, also, is distributed through the mass of black liquid. When the results do agree with the actual fat present, it is either due to an allowance made in calibrating the neck, or else to some casein being taken up by the floating fat that is measured at the top of the tube.

The white crystalline sediment I find to be principally sulphate of lime. The process is in principle the same as the Werner-Schmid process, which came out the previous year. Only, instead of artificially boiling the milk with hydrochloric acid, advantage is taken of the heat, naturally produced, on mixing milk with sulphuric acid. And then, instead of dissolving out and weighing the fat then set free, it is measured, after being driven together by a centrifugal apparatus. When working at the Schmid process in 1888, I tried the effect of using sulphuric acid, instead of hydrochloric acid; with benzoline afterwards to extract the fat, ether not being admissible. I found that after mixing the milk and acid, the fat is not all at once set free; for if the mixture be cooled five minutes after mixing, then another sample be cooled ten minutes after mixing, and a third sample be left to cool naturally, most fat is given by the third sample, least by the first sample.

Leaving the mixture to cool, I did not get all the fat actually present in the milk; hence, I then concluded that sulphuric acid destroyed some fat. Though not a good laboratory process, the Babcock method is, in my opinion, the best, cheapest, simplest, and most rapid dairy method of determining fat in milk. The use of strong, almost boiling, sulphuric acid is, however, somewhat dangerous.

In my hands, the process altogether failed for sweetened condensed milks. For much of the work, and for the diagrams shown to-night, I am indebted to my assistant, Mr. W. N. Yarrow.

#### DISCUSSION.

Mr. H. Droop Richmond thought the method described showed up very badly when compared with the Leffmann and Beam method. It seemed to have a considerable number of drawbacks in manipulation, which were not shared by the latter. But that was a comparatively unimportant point, when it was considered that the results obtained with the Babcock process by Mr. Stokes were inaccurate, while those quoted by the President, by the Leffmann and Beam method, were substantially exact. He was inclined to give every preference to the latter method.

Mr. Woosnam stated that he had recently made some experiments with the Babcock process, but the machine he used had niches for 30 bottles instead of 4. The results were unsatisfactory, and very similar to those obtained by Mr. Stokes. He did not think that sulphuric acid was a fit substance to be put into the hands of dairymen or others unskilled in manipulation.

The President thought that the Adams process was very difficult indeed to beat; it was the standard by which other methods were to be judged. But if a method entailing less trouble, and by which quicker determinations could be made, were brought out, he had no doubt that it would be welcomed by public analysts.

Mr. Stokes explained that instead of heating the tube artificially, it was heated by the mixture of sulphuric acid with milk.

Mr. Sidney Harvey thought that as the Babcock machine had no cogwheels it was the better of the two.

The President stated that Messrs. Leffmann and Beam only claimed for their process the improved method of liberating the fat.

**Resume of a Research on the Acids of Butter. Emil Koefoed.** (*Bulletin de l'Academie Royale Danoise*, 1891.) 785 grammes of a butter fat giving 15.1 c.c., Reichert figure (by Nilson's modification *Z. f. Anal. Chem.* 28, 175), were saponified with 200 grammes caustic soda in 500 c.c. of water; the soap was decomposed by 300 grammes of sulphuric acid diluted with 500 c.c. of water, and the liquid boiled under an inverted condenser till the soap was all decomposed, a current of carbon dioxide being passed through the flask. The fatty acids (720 grammes) were filtered, and the aqueous filtrate shaken three times with ether, which, on distillation, left 6 grammes of acids smelling like butyric. This extraction with ether was proved to have removed the whole of the organic acids.

The 6 grammes constituted Portion I.



The 720 grammes of acids left on the filter were distilled under 30 mm. pressure. The acids distilling between 93° and 200° weighed 54 grammes, and constituted Portion II.

The remaining acids were dissolved in 500 grammes of alcohol of 95° Tralles, and were several times crystallized from this medium; 100 grammes were thus obtained.

The whole of the alcoholic filtrates (about 4 litres) were, after the addition of 30 grs. of acetic acid, treated with an alcoholic solution of 600 grammes of crystallized lead acetate. The precipitate was collected after 24 hours on a filter, washed with alcohol, and air dried. The acids were then set at liberty by boiling with hydrochloric acid, and weighed 314 grammes, which, with the 100 grammes obtained by crystallization, formed Portion III.

The filtrate was made faintly alkaline with ammonia, and a small quantity of a semi-fluid lead salt separated, probably Gottlieb's oxyoleate of lead. This was boiled with hydrochloric acid, and the acid thus obtained dissolved in ammonia, and its barium salt precipitated by barium chloride. This formed Portion IV.

From the filtrate the alcohol was removed by distillation, and the fatty acids transformed into barium salts as above. These constituted Portion V.

The Portions were then examined.

*Portion V.* The barium salts were boiled successively with acetic ether and chloroform. From the acetic ether solution, oleate of barium separated on cooling. This was re-crystallized from 80 per cent. alcohol, and then gave the following figures:—

|    |     |     | Found  |     | Calculated for barium oleate. |     |       |
|----|-----|-----|--------|-----|-------------------------------|-----|-------|
| Ba | ... | ... | 19.38% | ... | ...                           | ... | 19.59 |

The chloroform solution gave, after cooling and filtering, on the addition of four volumes of ether, a white amorphous precipitate, which, on drying, became a brown, gummy amorphous mass.

The figures of analysis were as follows:—

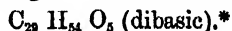
|    |     |     | Found |     | Calc. for Ba. (C <sub>15</sub> H <sub>27</sub> O <sub>4</sub> ) <sub>2</sub> |     |       |
|----|-----|-----|-------|-----|--|-----|-------|
| C  | ... | ... | 52.99 | ... | ...  | ... | 54.80 |
| H  | ... | ... | 7.51  | ... | ...  | ... | 7.98  |
| Ba | ... | ... | 20.07 | ... | ...  | ..  | 20.24 |

The author regards this acid as C<sub>15</sub>H<sub>28</sub>O<sub>4</sub>. It easily decomposed, as after some time its barium salt becomes insoluble in chloroform.

*Portion IV.* This is insoluble in ether, acetic ether and chloroform. The analysis is:—

|         |     |        |     |         |     |          |
|---------|-----|--------|-----|---------|-----|----------|
| C 56.43 | ... | H 8.43 | ... | O 12.69 | ... | Ba 22.45 |
|---------|-----|--------|-----|---------|-----|----------|

The author assigns the following formula to this acid:—




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\* Probably a mixture.—*Ab.*

*Portion III.* This portion was fractionated under 30 mm. pressure; Bruhl's receiver (*Ber.* 1888, 3389) being employed.

|                            |   |      |   |      |
|----------------------------|---|------|---|------|
| Fractions were collected:— | A | 200° | — | 230° |
|                            | B | 231° | — | 238° |
|                            | C | 240° | — | 242° |
|                            | D | 244° | — | 248° |
|                            | E | 251° | — | 255° |

The two last fractions were crystallized from a small quantity of alcohol.

The fractions B—E were fractionally precipitated by quantities of 25 c.c. of a normal magnesium acetate solution. The fractions were then boiled with hydrochloric acid, and the melting points of the acids taken; they were then transformed into silver salts, and the silver estimated. Fraction E<sub>i</sub> melted at 68°; after re-fractionating the melting point rose to 69°, and the silver salt contained 27·57 per cent. Ag. (calc. for stearic acid 27·62 per cent.) E<sub>ii</sub> melted at 62°, and its silver salt gave 29·73 per cent. Ag. (calc. for palmitic acid 29·75 per cent.).

*Fraction E* was then principally palmitic acid with a small quantity of stearic acid. Arachidic acid was not detected.

*Fraction D* was also palmitic acid.

*Fraction C* (weighing 131 grammes) was dissolved in 700 grammes of alcohol, and deposited, after 24 hours, 31·5 grammes of solid acids, principally palmitic acid; the remainder was fractionally precipitated by magnesium acetate, seven fractions being obtained.

*Fractions C<sub>iii</sub>—C<sub>vii</sub>* were magnesium myristate; the acid fused at 53°, and the silver salt contained 32·22 per cent. Ag. (calculated for myristic acid 32·24 per cent.).

*Fraction B* still contained myristic acid; B<sub>iv</sub> and B<sub>v</sub> were, however, lauric acid, for the acid melted at 43·5°, and the silver salt contained 35·35 per cent. Ag. (calculated for lauric acid 35·18 per cent.).

*Fraction A* was neutralized with ammonia, and fractionally precipitated by 5 portions of 20 c.c. of normal alcoholic silver nitrate. A<sub>iii</sub>—A<sub>v</sub>, corresponded to silver caproate.

*Portion II.* This was fractionated as fraction III A by means of 10 portions of silver nitrate. These were washed with alcohol, boiling water, and again alcohol, and air dried.

*Fraction 4* contained a percentage of silver corresponding nearly to silver caprylate; it was, therefore, refractionated, and a series of precipitates were obtained corresponding exactly to silver caprylate.

*Fractions 5—10* were chiefly silver caproate. In order to decide whether this was normal caproic acid or isobutylacetic, the author determined the solubility of the calcium salt. 100 c.c. of water at 17·5 dissolved 2·58 grammes of anhydrous calcium salt

Lieben (*Ann.* 165, 118) has shown that at 18.5° 100 c.c. of water dissolves 2.707 grammes of normal calcium caproate and 11.3 grammes of calcium isobutylacetate.

Butter, therefore, contains normal caproic acid.

*Portion I.* This was principally butyric acid. The silver salt, after crystallization from water, gave 55.27 per cent. Ag. (calculated for butyric acid, 55.38 per cent.)

Grünzweig (*Ann.* 162, 215) has already shown that the butyric acid in butter is normal.

The butter then examined contained 91.5 per cent. of fatty acids, of which the percentage composition is as follows :—

|                     |                      |     |     |   |         |
|---------------------|----------------------|-----|-----|---|---------|
| Oleic Acid          | ...                  | ... | ... |   |         |
| Acid of the formula | $C_{16}H_{32}O_4$    |     |     | } | .. 34.0 |
| " "                 | $C_{29}H_{54}O_6(?)$ |     |     |   |         |
| Stearic Acid        | ...                  | ... | ... |   | 2.0     |
| Palmitic Acid       | ...                  | ... | ... |   | 28.0    |
| Myristic Acid       | ..                   | ... | ... |   | 22.0    |
| Lauric Acid         | ...                  | ... | ... |   | 8.0     |
| Capric Acid         | ...                  | ... | ... |   | 2.0     |
| Caprylic Acid       | ...                  | ... | ... |   | 0.5     |
| Caproic Acid        | ...                  | ... | ... |   | 2.0     |
| Butyric Acid        | ...                  | ... | ... |   | 1.5     |
|                     |                      |     |     |   | 100.0   |

H. P. R.

**A New and Delicate Indicator for Alcoholic Solutions. S. Ruhemann.** (*Jour. Chem. Soc.*, lxi, 286).—The author suggests the use of the imide of dicinnamyl-phenylazimide as a delicate indicator with alcoholic solutions; the change is from red (acid) to purple (alkaline), and the colour is intensified by heating; it can be used to determine the small amount of alkali dissolved from glass by alcohol. The blue (purple) alkali salts are decomposed gradually by water, the ammonium salt being especially unstable. The indicator is best prepared by adding the calculated quantity of bromine (2 mols), to ethyl cinnamate dissolved in chloroform; the solvent is evaporated, and the resulting mass quickly heated with twice its weight of phenylhydrazine; after the violent evolution of gas has ceased, the semi-solid product is shaken with dilute hydrochloric acid, and filtered; through the filtrate is passed a current of air, warming at the same time. A red precipitate of the imide is formed, which is washed with water and crystallized from hot glacial acetic acid.

A mere trace of the indicator is required, as its solubility in alcohol is very slight; the alkaline salts are readily soluble in this menstruum.

H. D. R.

**Contributions to the Determination of Nitrogen and Albuminoids in Milk and its Products.** L. Carcano. (*Stazioni Sperimentali Agrarie Italiane*, xxii. 260.)—The author has compared the methods of Dumas and Kjeldahl for the estimation of nitrogen in milk and cheese, and that of Ritthausen for the determination of albuminoids in milk.

The average of his results are:—

|        |            | Ritthausen.    | Dumas.      | Kjeldahl.   |
|--------|------------|----------------|-------------|-------------|
|        |            | % Albuminoids. | % Nitrogen. | % Nitrogen. |
| Milk   | 4 samples  | 3.951          | .6044       | .5964.      |
| Cheese | 10 samples | —              | 4.927       | 4.901.      |

H. D. R.

[NOTE BY ABTRACTOR.—The percentages of nitrogen in milk, multiplied by 6.38, the factor for casein and albumin given by Sebelein, give 3.856 and 3.805 % albuminoids respectively. As the whole of the nitrogen is not contained in the precipitate by Ritthausen's method, it follows that the latter gives too high results. The factor given by Sebelein is based on experiments of Hammarsten, and other Scandinavian chemists, and has lately been confirmed by Chittenden and his fellow-workers.]

**Is Saccharin Injurious?** (*From a Bill on Wine, before the German Parliament.*)—The views concerning the physiological action of saccharin are at present much divided, as the following abstracts from literature will show: According to Stutzer (*Saccharin*, Leipzig, 1885), and Aducco and Mosso (*Gaz. delle cliniche di Torino*, 1886, 14 and 15), saccharin is not hurtful. Millardet states that the action of pepsin upon albumin is but little affected by it, nor is that of pancreatin upon casein, whilst that of pancreatin upon starch is much impeded, a ten-fold amount of pancreatin being necessary to dissolve a given quantity of starch in the presence of saccharin, than without the latter (*V. der Nahrungs und Genussmittel*, 1888, p. 44). According to Girard, saccharin is not harmless after long continued use; it produces indigestion and is not excreted by the kidneys (p. 387), whilst Pavy is of opinion that saccharin is harmless and most valuable in diabetes (p. 387). Experiments by Plugge show that a 0.3 p.c. solution of saccharin entirely prevents the action of ptyalin, and retards that of pepsin and pancreatin (1889, 319). E. Gans, L. C. Wooldridge, Th. Stevenson, A. Petschek, and T. J. Zerner regard saccharin as harmless (458). F. Jessen states that "soluble" saccharin is without influence upon the action of ptyalin and but slightly retarding upon that of pepsin, and that the utilisation of food is not affected even by large doses. K. B. Lehmann declares it to be unobjectionable from a hygienic point of view, but its substitution for sugar should be allowed only after notice to the consumer (1890, p. 186 and 187.)

According to A. Stutzer, commercial saccharin contains about 40 per cent. of parasulphamidobenzoic acid, which disturbs digestion. Salkowski states the amount of the para-acid to be, in the older samples up to 60 per cent., in the newer ones 33 p.c.,

whilst "soluble" saccharin contains about 26 p. c. He could not trace any injurious effects upon the human organism (1887. p. 457.)

In addition to these opinions, there are a number of reports of medical and other societies, and of various governments, referring to the use of saccharin in articles of food. The Comité Consultatif d'hygiène publique de France reported on August 13th, 1888, that saccharin must not be regarded as a food, and that it could not be used as a substitute of sugar. Its use prevented or retarded the digestion of starchy and albuminous foods, and produced a profound disturbance of the organs of digestion and caused dyspepsia. It therefore recommended that the use of saccharin in articles of food should be prohibited (*Ver. d. K. Gesundheitsamts*, 1888, 608.)

The Royal Academy of Medicine of Madrid declared that the addition of saccharin to food should be regarded as an adulteration and that the importation of articles containing it should be prohibited (1889, 319.) The Hungarian Sanitary Council also recommended, in 1889 that the use of saccharin in food be prohibited, first, because it is not a sugar, but might be used by the public as such; second, because it had no food value; thirdly, because it was liable to produce disturbances of digestion on long-continued use; and, lastly, on account of the probability that it would be used for fraudulent purposes (1889, 684). In the opinion of the Society of Bavarian Chemists (Meeting on May 16th and 17th, 1890), all articles of food, which owe their sweetness wholly or partially to saccharin, and which are not declared by the vendor to contain it, are to be regarded as adulterated (*Nahrungs und Genussmittel*, 1890, 187). The Austrian Sanitary Council considers saccharin to be harmless both to the healthy and to diabetic patients, but its use in food should be held to be an adulteration (*Gesundheitsamts*, 1890, 251).

The International Congress of Agriculture and Forestry, held in Vienna in September, 1890, passed a resolution, recommending that saccharin and similar sweetening agents should be allowed to be sold only by apothecaries upon physicians' prescriptions (1891, p. 118). According to a Spanish Cabinet order of April 3rd, 1889, saccharin is to be regarded as a drug, and articles of food may not contain the same, nor is their importation into Spain permitted (1889, p. 575). The Royal Académie de Médecine of Rio de Janeiro recommends the prohibition of the importation of saccharin into Brazil, as an article injurious to health (*Rev. intern. des falsif.*, 1889, p. 146). By Royal Order of September 29th, 1889, the importation and production of saccharin was prohibited in Italy, and this order passed into law on May 15th, 1890 (*Ver. d. K. Gesundheitsamts*, 1890, p. 481). A further order was made in August, 1890, forbidding the use of saccharin in wine. In Russia the use of saccharin is prohibited, except for medicinal purposes (p. 723). Also Portugal prohibits the importation of saccharin. A Belgian regulation of December 10th, 1890, renders it incumbent upon the vendors of articles of food containing saccharin to declare the use of the same (*K. Gesund. A.*, 1891, p. 337).

The question has also occupied the attention of the German Government and experiments upon dogs have been made, but no injurious effect could be proved. On this

account the Government in question does not think that the use of saccharin should be absolutely prohibited in articles of food or drink, especially as for diabetic patients the article is doubtless a valuable one. But in order that the article be not used for purposes of fraud and deception in commerce, its use for sweetening wine is recommended to be prohibited, unless a declaration as to its presence be made. (*From the Zeitschr. f. angew. Chemie*, May, 1892.) O. H.

**A Method of Discriminating between Natural and Artificial Water-marks.** **W. Herzberg.** (*Mitt. Königl. tech. Versuchs.*, 1892, x., 45, through *Chem. Zeit.*).—The water-mark in papers is produced by the impression of the characters constituting it upon the surface of the paper. When this is done during the process of manufacture of the paper, the resulting water-marks may be termed "natural," while if it be caused by pressure on a finished paper it may be described as an "artificial" water-mark. The two kinds may be distinguished by immersing the paper in strong caustic soda solution, e.g., 60 grms. of caustic soda and 200 c.c. of water. The "natural" water-mark becomes more noticeable by this treatment, while the "artificial" water-mark vanishes. The cause of this difference of behaviour is that the "natural" water-mark consists of a portion of the paper which is actually thinner than the surrounding parts, whereas in the case of the "artificial" water-mark the thickness of the paper was originally the same at that spot as at any other, and the action of the caustic soda swells the compressed fibre to its former dimensions. B. B.

**The Quantitative Separation of Silver and Lead.** **R. Benedikt and L. Gans.** (*Chem. Zeit.* 1892, xvi. 181, 182).—The method depends upon the fact that dilute nitric acid decomposes lead iodide, but does not attack silver iodide. Potassium iodide in excess is added to the solution containing both metals, and the resulting precipitate digested with dilute nitric acid, which must, of course, be free from chlorine. The presence of other metals of the same group, with the exception of mercury, does not interfere. Test analyses, made on known mixtures of the nitrates of lead, silver and copper, gave satisfactory results. The process, as applied to the determination of silver in argentiferous lead, is carried out as follows:—Ten to fifty grms. of the metal, according to the amount of silver it is supposed to contain, are dissolved in dilute nitric acid, containing tartaric acid to keep the antimony that may be present in solution, the solution diluted with boiling water, filtered and the filtrate diluted to 300 to 500 c.c., allowed to cool, then treated with 10 c.c. of a 10% solution of potassium iodide, warmed on the water-bath, and the residue of silver iodide collected and weighed in the usual manner. The percentage of silver in galena can also be determined by this method, the mineral being oxidised by nitric acid containing tartaric acid, and the solution treated with potassium iodide as before. A table is given in the original paper, showing the method to be fairly concordant with the dry assay for antimonial crude lead, ordinary crude lead, desilverized lead, and galena. B. B.

**The Composition of Coffee "Extracts."** **A. Domergue.** (*J. Ph. Chim.* 1892, xxv. 243, through *Chem. Zeit.*)—Coffee "extracts" or "essences" differ in composition according to their mode of preparation. One method consists in distilling the roasted and ground coffee with water, and thus obtaining a colourless distillate the odour of which recalls that of coffee, and which is turbid with a little essential oil. The residue in the retort is filtered and mixed with the distillate, thus forming an "extract." It does not contain all the extractive matter of the coffee, and when diluted with the appropriate amount of water is not the same colour as the freshly prepared liquid. In order to remedy this defect, caramel is added as well as strong alcohol, in order to preserve it. The author has examined six extracts, the results of which are given below. Samples A and B were prepared in the laboratory.

|                          | A.    | B.    | C.    | D.    | E.   | F.    |
|--------------------------|-------|-------|-------|-------|------|-------|
| Extract dried at 100° C. | 13·7  | 17·6  | 41·01 | 27·2  | 30·1 | 19·26 |
| Ash .. .. .              | 0·61  | 0·79  | 4·3   | 3·1   | 1·4  | 1·83  |
| Caffeine .. .            | 0·106 | 0·105 | 0·060 | 0·040 | 0·05 | 0·096 |

The samples C, D, and E have been coloured with caramel.

Probably the best method of ascertaining the value of an extract consists in the determination of the caffeine, although it is to be noted that even samples A and D only contained about 1/10th of the amount of caffeine which is contained in an equal weight of coffee. No rule can be laid down as to what should constitute a normal coffee "extract."

B. B.

**The Influence of Saccharine Matter in the Fodder upon the Composition of Milk Fat.** **A. Meyer.** (*Milch. Zeit.*, 1892, xxi. 49, through *Chem. Zeit.*)—The author is of opinion that the composition of milk fat is largely dependent upon the nature of the fodder, notably in the case of easily soluble carbo-hydrates, which tend to raise the proportion of liquid fatty acids, and thereby depress the melting point of the fat as a whole. The following are his conclusions in detail:—(1) A not unimportant quality in butter, as far as its commercial value is concerned, is its consistency. This is especially true in the English market, where soft butters appear to be less esteemed than those of normal consistency. (2) The consistency of butter, although influenced by the process of manufacture, mainly depends on the melting point of the butter fat. (3) The melting point of butter fat is obviously dependent on its composition, so that the presence of a considerable amount of volatile fatty acids, or of non-volatile liquid fatty acids, is disadvantageous. (4) The melting point of butter fat is affected both by the character of the individual animal yielding it and by the breed to which it belongs, and may be influenced by the selection of particular breeds and by the choice of individuals belonging to them. (5) The melting point of butter fat is also largely dependent upon the fodder, and easily digestible carbo-hydrates, especially saccharine substances, tend to lower the melting point of the butter, while fodder poor in soluble carbo-hydrates has the opposite effect.

B. B.

**The Simultaneous Precipitation of Copper and Antimony by the Electric Current.** W. Hampe. (*Chem. Zeit.*, 1892, xvi. 417-418.)—All commercial samples of copper, prepared electrolytically, which the author has examined, contain small quantities of antimony, ranging from 0·007 to 0·02 per cent. The reason for this is to be found in the practice of allowing the sulphuric acid, used as an electrolyte in the purification of argentiferous copper in the wet way, to circulate repeatedly through the depositing tank until it becomes comparatively rich in impurities. By frequent renewal of the liquor the co-precipitation of the antimony can be minimised, though it cannot be entirely avoided. The same action occurs in the electrolytic determination of copper from a solution containing antimony, even when the current is interrupted immediately precipitation is complete. Experiments made with copper solutions containing known amounts of antimony showed that under favourable circumstances as much as 0·02 per cent. might be precipitated.

B. B.

## LEGAL.

## HIGH COURT OF JUSTICE.\*

*Tuesday, May 31, 1892.*

Queen's Bench Division. (Before the LORD CHIEF JUSTICE).

JOHNSTONE v. TILDEN AND OTHERS.

*Mr. Jelf, Q.C., Mr. Pocock, and Dr. B. O'Connor* (instructed by Mr. J. P. Godfrey) appeared for the Plaintiff.

*The Solicitor-General (Sir Edward Clarke, Q.C.) and Mr. Boydell Houghton* (instructed by Messrs. Markby, Stewart, and Co.), appeared for the Defendants.

(*Transcript from Shorthand Writer's Notes*).

The Solicitor-General:—Will your Lordship forgive my interposing for the moment during the hearing of another case to relieve your Lordship's list of a case which we shall not have to trouble the jury with? It is the case of *Johnstone v. Tilden and others*, and my learned friend Mr. Jelf, who appears for the plaintiff, wishes to say a few words.

The Lord Chief Justice:—Certainly.

Mr. Jelf:—If your Lordship thinks that I am not unduly interfering with the case that is now on, to suit the Solicitor-General and my convenience, I should like to mention this case now. I appear for the plaintiff, Dr. Johnstone, with my learned friends Mr. Pocock and Dr. O'Connor. It is an action brought by the Doctor against the Institute of Chemistry of Great Britain and Ireland, represented here by my learned friend the Solicitor-General. The action was brought to prevent the Institute from persevering in excluding him from being a Member and Fellow of the Institute upon a certain charge of unprofessional conduct which had been made against him. My Lord, I have very carefully

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considered the facts, and the evidence on which this case was sought to be based, and although my client was very desirous of clearing his character as much as he possibly could, I pointed out to him that their Charter gave the Institute very large powers, so long as they were acting in good faith and in accordance with their rules, in deciding rightly or wrongly on the matters brought before them. My client has, I hope wisely, placed himself in my hands in the matter, and in accordance with what has passed between the Solicitor-General and myself, we have agreed, with your Lordship's permission, to deal with the case by making a short statement on each side. On the part of the plaintiff, I desire to withdraw unreservedly any suggestion that these gentlemen have been acting otherwise than in good faith and in accordance with the rules of the Institute. On the other hand, I am glad to say that the Solicitor-General sees his way to saying this on behalf of the gentlemen whom he represents: "That their action was founded entirely on their view of the professional conduct of the plaintiff on a single occasion, and involved no imputation upon his character or professional capacity." Two views might possibly be taken of the question that was at issue; but looking to the circumstances of the case, and, it seems to me, the very handsome way I have been met by the Solicitor-General, with the consent of his clients, I think it would be extremely unwise for my client to fight for more than he has received. Under these circumstances we have agreed, with your Lordship's consent, to withdraw the record, and meanwhile the plaintiff undertakes to give up any title he might have had to be a Fellow or a Member of the Institute, and to hand over what perhaps I cannot say that my client is entitled to keep, but no doubt he will do what is right,—he will not persist in representing himself as a member of the Institute, and he will hand over his documents.

The Solicitor-General :—I am much obliged to your Lordship for allowing me to interpose. Representing the authorities of the Institute of Chemistry, my only desire is to make it perfectly clear, and it is their only wish to make it clear, that they acted throughout deliberately and in the exercise of the deliberate judgment vested in them, and according to the rules of the Institute to which the plaintiff himself belonged. The words my learned friend has read are words that I agree to; I agree that there might be some controversy and difference of opinion as to the action of the plaintiff himself, which was brought under the notice of the defendants, but it was carefully considered by them; they took the course they were bound to take in the interests of their profession, and I am glad to have the opportunity of saying not only that they have acted regularly in the manner, but they are anxious their action should not be taken to carry with it an imputation which it really ought not properly to bear. It was a question of professional conduct in a single instance and their action upon it, and that action they were obliged to notify. In this case, my Lord, we have agreed to the record being withdrawn with your Lordship's permission.

Mr. Jelf :—And no costs.

The Lord Chief Justice :—I can only give effect to the desire of the parties and the record may be withdrawn.

## CORRESPONDENCE.

BEECHFIELD,

WALTHAMSTOW,

June 18th, 1892.

*To the Editors of THE ANALYST.*

GENTLEMEN,

Dr. Frankland, in his letter in the June number of THE ANALYST, evades the true issue between us. My complaint was, that he stated my analyses to be incomplete, as they gave "no information regarding the quantities of organic elements in the samples," and further, that "failing *these data*, it is impossible to form any trustworthy opinion as to the quality of the water from a hygienic point of view." (*Vide* letter from Dr. Frankland, ANALYST, p. 90.)

It is perfectly plain that Dr. Frankland means by "organic elements" the "organic carbon and organic nitrogen," not the nitric nitrogen. His insinuation that my analyses consisted only of the data enumerated in his letter to you, instead of the details given in my paper, is neither correct nor to the point.

Those who were present when I laid the matter before the Society will remember that I placed upon the table copies of the printed report sent to Dr. Frankland, and they can bear me out when I repeat that the details were correctly described in my communication.

Dr. Frankland suggests that I am guilty of equivocation as regards the "nitrogen as nitrates," and implies that if I had estimated this "trustworthy datum" he would have been able to forgive the omission of the organic elements. It is true that I only tested qualitatively for nitric acid, but this datum had nothing whatever to do with the conclusion at which I was forced to arrive as to the inefficient purification of the samples of water in question. In common with almost every other analyst, I attach the greatest possible value to the determination of nitrates in samples of water, but, in the case of a water-supply from the river, the variation in the nitric nitrogen is so small that in any case it would not affect the conclusion drawn from the amount of free and albuminoid ammonia and of oxygen absorbed.

The statement in the last paragraph of Dr. Frankland's letter affects all chemists who analyse and report upon samples of water. If it were true, as there stated, that in cases of importance, as in the water-supply of towns, the only reliable method is the combustion process, it would be as well for the Water Committee to be re-constituted to inquire whether any changes have been made in the process in question which justify its being raised from the position to which it was relegated by that Committee in 1881.

I am, &amp;c., yours,

LEO TAYLOR.

# THE ANALYST.

AUGUST, 1892.

## SUMMER EXCURSION.

The arrangement of last year, that the Society should make London the starting point of their summer excursion, having proved so successful, it was decided to adopt a similar course this time. Dr. Ashby had some time since expressed himself desirous of entertaining the Society during a portion of the day, and in order to enable the party to avail themselves of his kind invitation, it was determined that the excursion should again take the form of a river trip--starting above Reading, exploring the upper reaches of the Thames, and returning to Dr. Ashby's house at Reading. The party (numbering some 30 members and friends, and including a fair proportion of ladies), met at Paddington and travelled to Goring, where a steam-launch was waiting to convey them to Wallingford. Arriving here, they sat down to an excellent luncheon at the Lamb Hotel, followed by some humorous speeches from the President, Mr. Allen and Mr. Cassal. The launch was again boarded and the party steamed down to Reading, where carriages were in readiness to convey them to Dr. Ashby's residence. An out-door entertainment in the form of a garden party was provided; several hours were agreeably spent in perambulating Dr. Ashby's charming and picturesque grounds, and in enjoying the refreshments so liberally provided. A vote of thanks to Dr. and Mrs. Ashby for their kindness was proposed and carried with acclamation, after which the party were conveyed to Reading station, whence they took train for Paddington, arriving there about 11 o'clock. The weather was all that could be desired, and a thoroughly enjoyable day was spent. Several photographs of the party were taken by Messrs. Chattaway and Stansell.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A Special Meeting of the Society was held on Thursday, 30th June, at the rooms of the Society of Arts, John Street, Adelphi, the President (Mr. Otto Hehner) in the chair.

The following gentlemen were proposed as Members :--Messrs. Gustave Antcnio Abrines, F.C.S., E. J. Bevan, and John Bate Nickolls.

Dr. A. P. Aitken, 8, Clyde Street, Edinburgh, and Mr. Frederick William Tompson, F.C.S., Stapenhill Road, Burton-on-Trent, were duly elected Members of the Society.

Mr. J. Williams, Government Laboratory, Georgetown, Demerara, British Guiana, was duly elected an Associate.

Mr. Allen temporarily took the chair whilst the President read a paper "On the Estimation of Olein," which was followed by a discussion.

The President having resumed the chair, Mr. A. H. Allen read a paper entitled "Experiments on the Alkaloid of Tea," and, after the paper had been discussed, Dr. Teed read the following paper:—

#### THE DETECTION AND ESTIMATION OF MINUTE QUANTITIES OF LEAD IN THE PRESENCE OF COPPER AND IRON.

By FRANK L. TEED, D.Sc.

I propose first to refer to the detection of lead in sulphuric acid. The usual method is by dilution with water, but I found, some years ago, that by adding hydrochloric acid to the sulphuric acid, and keeping it cold, a much smaller quantity of lead could be detected than by adding water, or even by adding water and subsequently an equal volume of absolute alcohol. The lead is precipitated as chloride as a peculiar pearly opalescence. I patented this process for the purpose of removing lead from sulphuric acid, which it does perfectly, but sulphuric acid manufacturers assure me that there is no commercial value in any process that would effect such a result. Although leaving something to be desired as a patent, the process is still of use as a test on account of its delicacy. It can be applied to the detection of minute quantities of lead in organic substances. Take, for instance, a substance which is generally, I may say invariably, contaminated with lead—tartaric acid. The lead is a little difficult of detection by the ordinary process, because sulphide of lead, as we know, is more or less soluble in tartaric acid. If the tartaric acid is ignited, a large proportion of the lead is, of course, lost, but some is left, and there is sufficient in the small quantity of ash, if digested with pure sulphuric acid, to show the characteristic reaction on the subsequent addition of hydrochloric acid. While on the use of hydrochloric acid as a test for lead in sulphuric acid, I may mention that nitric acid is also a test for lead in sulphuric acid; but it is not nearly so delicate as hydrochloric acid. If to a sample of commercial sulphuric acid which is very rich (*i.e.*, very impure) in lead, nitric acid is added, the lead mainly settles out, but still, after treatment with nitric acid, lead can be detected by the addition of hydrochloric acid. Hydrochloric acid gas is insoluble in sulphuric acid, and if passed through strong sulphuric acid which is highly contaminated with lead, for an hour or more, nothing whatever happens, but if to that acid in a test tube a single drop of the solution of hydrochloric acid, or a crystal of common salt is added, the characteristic precipitate at once appears.

The main object of my paper was to draw attention to the difficulty of detecting and estimating minute quantities of lead in presence of copper and iron. There are certain temperance drinks, such as lemonade and soda water, which, in the process of manufacture, are liable to contain at least these three metallic impurities.

In the case of lemonade, the lead occurs partly in the tartaric acid used, and partly comes from the use, perhaps one ought to say abuse, of lead pipes for transferring the charged solutions; and the copper comes from the copper cylinders (although tin-lined) in which the drink is charged with carbonic acid. Hence the difficulty arises of detecting a highly poisonous metal like lead, in the presence of a mildly poisonous metal like copper, and a non-poisonous metal like iron. The most delicate reaction for both lead and copper is, I believe, the precipitation as sulphides, either by sulphuretted hydrogen or ammonium sulphide. The amounts present can, of course, be estimated colorimetrically by comparison with known quantities. I find the sulphide reaction far more delicate in the case of copper than the ferro-cyanide reaction. I do not think the hundredth of a grain of copper in a gallon of liquid could be detected by means of the ferro-cyanide reaction without concentration, but ammonium sulphide would easily detect it. The objection to this reagent is that it does not distinguish between lead and copper. To effect this distinction I simply make use of the well-known fact that sulphide of copper is soluble in cyanide of potassium, whereas sulphide of lead is not. To perform a determination:—Place a measured quantity of lemonade, or other liquid, in a cylinder or white basin. Add a few c.c. of ammonia and a little cyanide of potassium, then add a minute quantity of ammonium sulphide. Down comes the lead, but not the copper. Then imitate the colour by known quantities of lead precipitated under similar conditions. Iron does not at all interfere with the test. If an iron salt is added to lemonade, for instance, and made alkaline with ammonia, the iron is kept in solution by the tartaric acid, and on addition of cyanide of potassium is converted into a ferro or ferri-cyanide, not precipitable by ammonium sulphide. In the case of liquids not containing tartaric acid, it is easy enough to add a little in the event of iron being present.

#### DISCUSSION.

Mr. Bertram Blount said that with reference to the general question of testing for lead in small quantities, that there was one test, the merits of which Mr. Allen and Mr. Harvey had done much to make known. He referred to the chromate test, which he constantly used for all purposes; it was not only exceedingly delicate if properly carried out, but also extremely characteristic.

Mr. Sidney Harvey said that in water containing a fiftieth part of a grain of lead per gallon, the metal could be precipitated by bichromate of potash. If allowed to stand for 12 hours the water could be poured off to the last drop, and the chromate of lead could then be advantageously stirred up with a little distilled water and turned into a smaller vessel, say a half-inch test tube, when a precipitate visible both by colour and amount would quickly settle.

Mr. E. Russell Budden said he had found that when the chromate test was used in the presence of organic matter, a reduction always took place. For instance, in a case of testing for lead in lemonade, if one used the chromate test with the original liquid, and allowed it to stand for a time, in a great many cases, presumably from the fact of

tartaric acid or other reducing agents being present, a green chromium salt was produced, and the chromate precipitate was practically unobservable. He did not know whether any of the members had observed the same thing, but it had been an insuperable difficulty with him in applying the test in presence of organic matter. Whilst speaking of the chromate test, he would mention that he had adopted the method of observing it under different conditions of light to those usually recommended. He believed the usual method was to place the water in a cylinder or vessel of some kind to allow of settlement and decantation. He had found that if the test were observed in an ordinary light, very frequently a *minute* trace of lead escaped observation; but if the light were shed in such a way that an oblique beam fell through the liquid, all other light being excluded, a characteristic opalescence could be detected. He used a square box sufficiently large to contain a good sized flask, and so constructed that the light came only through an aperture in the upper part. By adopting this method, he was able to detect exceedingly minute quantities of lead in waters, quantities which, without these precautions, the method utterly failed to give any indication of. He had been worrying over this matter for a very long time, and had tried the experiment in presence of copper and other metals. In addition to the two or three metals mentioned by Dr. Teed, tin was occasionally present in artificial mineral waters; and he had also found traces of antimony. He believed the President could bear him out so far as the tin was concerned.

Dr. Teed, in reply, said that he was obliged, in testing lemonades, to abandon the chromate test for reasons similar to those mentioned by Mr. Budden. He would like to know whether Mr. Blount or any other member had personal experience with the chromate test in presence of tartaric acid or other organic matters, such as occurred in commercial lemonades. With regard to the presence of tin and antimony, they would not interfere with the test for lead, it being performed in an alkaline solution with ammonium sulphide as the precipitant.

Dr. Sykes read a paper "On a deposit found in Fermenting Vats," after which Mr. Richmond read the following paper:—

## LEFFMANN AND BEAM'S METHOD OF FAT ESTIMATION IN MILK.

### PART I.

By H. DROOP RICHMOND.

LEFFMANN and Beam (*THE ANALYST*, xvii., 83) have recently described a method, a modification of the Babcock centrifugal method, for fat estimation in milk.

Hehner (*THE ANALYST* xvii., 102) reports favourably on it; he presumes that the layer measured is not pure butter fat, but is a mixture of fat and fusel oil.

In the discussion on Hehner's paper, Allen was of opinion that in order to get accurate results the temperature should be taken into account; I pointed out that the factor used by Leffman and Beam (0.86) was probably obtained by dividing 0.89, the density of butter fat at 50° or 60°, by 1.032, the average density of milk.

I have lately, by the kindness of the President in lending me his machine, had the opportunity of investigating this method. I must withdraw my former opinion mentioned above, as I find that the temperature of the fat is about  $25^{\circ}$  to  $30^{\circ}$  when measured, and therefore, if pure butter fat, the density would be about 0.92, instead of 0.89; this is evidence that the layer measured is not pure butter fat.

My experiments may be divided into three series:—

- I. With bottles received from Messrs. Leffmann and Beam, graduated in 100 parts, and using ordinary fusel oil.
- II. With bottles made by Messrs. Müller and Co., 148, High Holborn, graduated so that 86 divisions = 1.475 c.c., and using ordinary fusel oil.
- III. With bottles as in II., and using pure amyl alcohol from Hopkin and Williams, 16, Cross Street, Hatton Garden.

They were compared with fat estimated by the Adams (A), Wanklyn (W), Schmidt (S), and Carter-Bell (C-B) processes, and, in the case of creams, the fat calculated by Vieth's table (V) (THE ANALYST, ix., 64).

Creams were analysed by measuring 10 c.c. in a 10 c.c. specific gravity bottle, diluting it to 50 c.c., and taking 15 c.c. of this mixture; the results were calculated by the following table:—

| Reading. | Percentage of cream. | Reading. | Percentage of cream. |
|----------|----------------------|----------|----------------------|
| 40       | 18.4                 | 70       | 34.8                 |
| 45       | 21.1                 | 75       | 37.6                 |
| 50       | 23.8                 | 80       | 40.4                 |
| 55       | 26.5                 | 85       | 43.2                 |
| 60       | 29.3                 | 90       | 46.0                 |
| 65       | 32.0                 | 95       | 48.8                 |

The results obtained were:—

#### Series I.

| No. |     | Fat.         |                |              |
|-----|-----|--------------|----------------|--------------|
|     |     | Gravimetric. | L and B.       | Error.       |
| 1.  | ... | 3.22         | 3.27           | + .05        |
| 2.  | ... | 3.36         | 3.53           | + .17        |
| 3.  | ... | 3.52         | 3.61           | + .09        |
| 4.  | ... | 3.58         | 3.53           | — .05        |
| 5.  | ... | 3.76         | 3.91           | + .15        |
| 6.  | ... | 3.36         | 3.44           | + .08        |
| 7.  | ... | 2.70         | 2.9            | + .20        |
| 8.  | ... | 3.68         | 3.83           | + .15        |
| 9.  | ... | 3.96         | 3.91           | — .05        |
| 10. | ... | .24          | .28            | + .04        |
| 11. | ... | .22          | .21            | — .01        |
| 12. | ... | .22          | .21            | — .01        |
| 13. | ... | .36          | .4             | + .04        |
| 14. | ... | 11.4         | 11.5           | + .1         |
| 15. | ... | 57.6 V       | 57.0           | — .6         |
| 16. | ... | 26.1 V       | 26.2           | + .1         |
| 17. | ... | 20.9         | { 20.8<br>21.3 | — .1<br>+ .4 |

All gravimetric determinations, unless otherwise stated, were obtained by the Adams method.

The results in Series I. are good; there is a tendency, on the whole, to obtain slightly higher figures by the centrifugal method. Unfortunately, the bottles used in this series were broken, and I have no means of testing the graduations.

Besides these, I have tested numerous milks and compared them with the calculated results; in no case did the error exceed 0.2 per cent.

### Series II.

#### Fat.

| No.     | Gravimetric. | L and B.  | L and B corrected. | Error. |
|---------|--------------|---|--------------------|--------|
| 18. ... | 2.42         | 2.65  | 2.49               | + .07  |
| 19. ... | 22.0         | 23.2  | 21.8               | — .2   |
| 20. ... | 29.4 V       | 31.7  | 29.8               | + .4   |
| 21. ... | 23.8         | 24.3  | 22.9               | — .1   |
| 22. ... | .24          | .35   | .33                | + .09  |
| 23. ... | 1.48         | 1.65  | 1.55               | + .07  |
| 24. ... | 2.18         | 2.4   | 2.25               | + .07  |
| 25. ... | 3.98         | 4.1   | 3.85               | — .15  |
| 26. ... | 5.04         | 5.45  | 5.12               | + .08  |
| 27. ... | 7.85         | 8.2   | 7.70               | — .15  |
| 28. ... | 11.80        | $\left\{ \begin{array}{l} 13.05 \text{ (10 c.c. milk)} \\ 12.9 \text{ (5 c.c. milk)} \end{array} \right.$ | 12.2               | + .4   |
| 29. ... | 22.9 V       |   | 12.1               | + .3   |
|         |              | 25.4  | 23.9               | + 1.0  |

The results in this case were too high by the centrifugal method, and were corrected by dividing by 1.065, which gave a satisfactory agreement.

A probable reason for this difference will be given later on.

### Series III.

Experiments were first made varying the quantity of the fusel mixture.

A cream was taken, which gave by the Schmidt method 21.4 per cent., and by the Adams 21.4 per cent; average, 21.4 per cent.

|         |                      | Divisions.             | Fat by table. |
|---------|----------------------|------------------------|---------------|
| 30. ... | 1 c.c. fusel mixture | 41.5                   |               |
| 31. ... | 3 c.c. " "           | 45.5                   | 21.2          |
| 32. ... | 5 c.c.               | 47.0                   |               |
|         |                      | 35.0 of a dark liquid. |               |

This 35 divisions was proved to consist essentially of fusel oil, and to equal 0.6 c.c. fusel oil, containing, however, a proportion of acid.

Subtracting, then, this quantity from the quantity added in the 5 c.c., we have in solution:—

|       |     |     |                        |
|-------|-----|-----|------------------------|
| in 30 | ... | ... | 0.5 c.c. in fusel oil. |
| " 31  | ... | ... | 1.5 c.c. " "           |
| " 32  | ... | ... | 1.9 c.c. " "           |



As the cream contained 21·4 per cent. fat, and the 10 c.c. weighed 1·010 grams, the fat should occupy 40·0 divisions, giving an excess of :—

|       |     |     | Found.        | Calculated. |
|-------|-----|-----|---------------|-------------|
| in 30 | ... | ... | 1·5 divisions | 1·8         |
| „ 31  | ... | ... | 5·5 „         | 5·4         |
| „ 32  | ... | ... | 7·0 „         | 6·8         |

These are almost in proportion to the quantity of fusel oil, as shown by the figures calculated from the mean ratio.

Another cream, containing 24·0 per cent. fat, gave figures as follows :—

|    |     |                      |                 |
|----|-----|----------------------|-----------------|
| 33 | ... | 1 c.c. fusel mixture | 47·0 divisions. |
| 34 | ... | 3 c.c. „ „           | 51·0 „          |

The fat should occupy 45·0 divisions, showing an excess of :—

|       |     |     |     | Found. | Calculated. |
|-------|-----|-----|-----|--------|-------------|
| In 33 | ... | ... | ... | 2·0    | 2·0         |
| „ 34  | ... | ... | ... | 6·0    | 6·1         |

The excess is in the same ratio.

When a substance is dissolved in a mixture of two immiscible solvents, it dissolves in each of them if the solutions are not saturated in the ratio of the maximum solubility of each, provided that combination does not take place.

To test this statement 10 c.c. of a solution of mercury chloride were taken and shaken with 15·1 c.c. of ether; after correcting for change of volume, it was found that 10 c.c. of ether contained 0·318 gram, and 10 c.c. of water 0·080 grams, or a ratio of 3·97 to 1·0.

The maximum solubilities are in water 7·4 grams. per 100 c.c., and in ether 30 grams. per 100 c.c., or a ratio of 4·05 to 1.

Skinner (*Jour. Chem. Soc.*, lxi., 339) finds ratios varying from 4·00 to 4·37 mean 4·16.

Calculating from the figures in No. 30-34 inclusive, the maximum solubility of fusel oil in fat should be 17·5 per cent., and in the acid mixture 5·9 per cent.

This is an extension of Henry's law of the distribution of a gas between a space and a liquid, and assumes that a substance in solution behaves like a gas; this is in accordance with recent theories of solution (*c.f. Ostwald's Solutions*).

The experiments quoted above furnish *a priori* evidence that after fusel oil, acid, and milk have been mixed as in the conditions of experiment, there is no free alcohol in solution; in connection with this may be noticed the following points :—

- (i.) Fusel oil and butter-fat are miscible in all proportions.
- (ii.) Sulphuric acid combines with alcohols, and fusel oil consists almost wholly of these latter bodies.

As the extension of Henry's law quoted above would not hold good, were free alcohol assumed to exist in solution, the fact that it does hold good by deduction shows that the

fusel oil has disappeared as such. The formation of amyl (propyl, iso-propyl, &c.), hydrogen sulphate is a possible reaction.

Experiments were made to test this assumption, and to confirm, if possible, the figure (5.9 per cent.) calculated for the maximum solubility in the acid mixture. Varying quantities of the fusel mixture were added to 15 c.c. of water, 9 c.c. of acid were poured in, and the mixture shaken; a hot mixture of 2 pts. water and 1 pt. acid was then added till the flask was full (total volume 28 c.c.), with results as follows:—

| Volume of fusel mixture. |     |     |          | Result.                         |
|--------------------------|-----|-----|----------|---------------------------------|
| 35                       | ... | ... | 3.2 c.c. | Small layer of black particles. |
| 36                       | ... | ... | 4.7 c.c. | Considerable separation.        |
| 37                       | ... | ... | 3.0 c.c. | Small layer of black particles. |
| 38                       | ... | ... | 2.5 c.c. | " " " "                         |
| 39                       | ... | ... | 3.5 c.c. | Separation of 4 divisions.      |
| 40                       | ... | ... | 3.8 c.c. | Considerable separation.        |

The limit of solubility is then 3.5 c.c. of the fusel mixture = 1.75 fusel oil; this gives a maximum solubility of 6.1 per cent., which is practically the same as the maximum solubility calculated.

The layers separating in 36 and 40 were examined; they were found to be very nearly soluble in water, about 10 per cent., however, being undissolved, and to give the water an intensely acid reaction; several of the layers of fat obtained in various experiments were also examined by shaking them with water, which always acquired a strong acid reaction, much greater than was given by butter-fat simply treated with strong acid.

These experiments greatly strengthen the view that amyl hydrogen sulphate is formed, which then distributes itself between the acid mixture and the fat in the ratio of the maximum solubility of each.

I have been unable, with the means and time at my disposal, to actually prove that amyl hydrogen sulphate is formed, and to determine its maximum solubility in butter-fat; but the evidence points strongly to the truth of the assumption that I have made, and it explains so satisfactorily the various phenomena observed, that I do not hesitate to adopt it.

The figure for the solubility of fusel oil (as amyl hydrogen sulphate) in the acid mixture would not hold good were the proportions of acid to water varied; and this affords an explanation as to why the results in Series I. differed from those in Series II. The bottles in Series I. were larger than in Series II., and more acid was constantly added in the former than in the latter, and the solubility of the fusel oil thereby increased; added to this, the volume of the acid mixture was also larger, and therefore a less quantity of fusel oil passed into the fat in Series I.

It is important, then, to have the bottles of the same size, or to add a constant amount of each of the re-agents. I have adopted as normal, bottles holding 28 c.c. and proportions, as follows: milk 15 c.c., fusel mixture 3 c.c., sulphuric acid 9 c.c., and for filling up the bottles a hot mixture of 2 pts. water to 1 pt. acid by volume.

In experiments 30 and 33, where 1 c.c. only of fusel mixture was used, it is worthy of note that the fat showed a tendency to solidify on cooling, while in the others it remained liquid till the close of the experiment.

A few experiments, which properly belong to Series III., were made before the importance of adhering strictly to the proportions was realized; as they were partially the means of leading me to search for the laws governing the volumes of fat, I give them:—

| No. | Gravimetric. | Fat       |            |
|-----|--------------|-----------|------------|
|     |              | L. and B. | Corrected. |
| 41. | 21.7 C.B.    | 21.6      | 20.3       |
| 42. | 23.2* V.     | 24.2      | 22.7       |
| 43. | 24.0 A.      | 24.5      | 23.1       |
|     | 23.7 W.      |           |            |
|     | 22.9 V.      |           |            |
| 44. | 21.4 A.      | 21.4      | 20.1       |
|     | 21.4 S.      |           |            |
|     | 20.5 V.      |           |            |

It is seen that the figure read direct from the table is much closer to the actual fat than that corrected by dividing by 1.065, and it was partly to seek an explanation of this that I commenced the experiments recorded above. As the number of creams in series I. and II. was only 7, and it was from the mean of these that the table was calculated by allowing for the decrease of density of the cream as the fat increased, and as the experimental error with creams is multiplied by 5 on account of the dilution, and, further, as only two creams in Series II. were analysed by Adams' method—one of which (No. 21) agreed better with the direct result than the corrected one—the discrepancy between series II. and III., viewed in the light of the discovery of previously unsuspected sources of error, did not seem so serious; it pointed, however, to the necessity of the revision of the table given above by exact experiments.

A comparison of the three series of experiments with Leffmann and Beam's original bottles, shows that Leffmann and Beam in six experiments have, practically, no average error. Hehner finds an average deficiency of 0.06 per cent. in seven experiments, while I (series I neglecting creams) find in fourteen experiments a mean difference of +0.08 per cent. These differences between the results of different operators are probably due to a difference in the average amount, and possibly strength, of acid added, and possibly also to a difference in the fusel oil used.

A series of results was now started, using bottles holding 28 c.c., and adding the re-agents in the proportions given above. Milks only are given in this table.

\* Experiments made on mixtures of this cream with skim milk show that it contained about 24 per cent. fat. Vieth's table is not accurate within 1 per cent.

## Fat.

| No.  | Gravimetric. | L. and B.             | L. and B. corrected. | Error. |
|------|--------------|-----------------------|----------------------|--------|
| 45.  | 3.48         | 3.75                  | 3.48                 | —      |
| 46.  | 2.42         | 2.6                   | 2.44                 | +0.02  |
| 47.  | 4.06         | 4.35                  | 4.09                 | +0.03  |
| 48.  | 3.09         | 3.35                  | 3.15                 | +0.06  |
| 49.  | 3.18         | 3.43                  | 3.22                 | +0.04  |
| 50.  | 3.23         | 3.45 } bottle 29 c.c. | 3.24                 | +0.01  |
|      |              | 3.45 }                |                      |        |
| 51.  | 2.08*        | 2.45                  | 2.30                 | +0.22  |
| 52.  | 3.45         | 3.67                  | 3.45                 | —      |
| 53.  | 3.54         | 3.8                   | 3.57                 | +0.03  |
| 54.  | 3.50         | 3.75                  | 3.52                 | +0.02  |
| 55.† | 4.47         | 4.95                  | 4.65                 | +0.18  |
| 56.† | 5.10         | 5.3                   | 4.98                 | —0.12  |
| 57.† | 2.08         | 2.32                  | 2.18                 | +0.10  |
| 58.† | 3.27         | 3.67                  | 3.45                 | +0.18  |
| 59.† | 3.72         | 4.1                   | 3.85                 | +0.13  |
| 60.  | 2.82         | 3.02                  | 2.84                 | +0.02  |
| 61.  | 3.56         | 3.72                  | 3.49                 | —0.07  |
| 62.  | .22          | .2                    | .19                  | —0.03  |
| 63.  | .20          | .25                   | .23                  | +0.03  |
| 64.  | 3.64         | 3.95                  | 3.71                 | +0.07  |
| 65.  | 4.19         | 4.3                   | 4.04                 | —0.15  |
| 66.  | 2.46         | 2.7                   | 2.53                 | +0.07  |
| 67.  | 3.25         | 3.45                  | 3.24                 | —0.01  |

The agreement is seen on the whole to be very good. There is, if anything, a tendency to be somewhat high, indicating that the factor used (1.065) is, perhaps, low. The factor 1.07 agrees rather better, but the difference is within the limits of reading. I have pointed out in the foot-notes that there is some explanation to be readily found for the larger discrepancies—*i.e.*, Nos. 51, 55-59 inclusive. The agreement between the fat found by this method and that gravimetrically determined, is as good on the whole as the agreement between duplicate gravimetric determinations obtained in ordinary commercial work, where extreme precautions are not taken to insure exactitude.

There are numerous sources of error, which I enumerate and discuss.

(i.) The milk is measured, not weighed, while the results are calculated as percentages by weight. Vieth (*THE ANALYST*, Vol. xvi., p. 90) has, however, shown that this source of error is very small.

\* This was a mixture of skim milk, cream, and water. The fat calculated from the proportions used should be 2.25. This makes me ascribe the large difference to an error in the gravimetric determination.

† These 5 milks were also somewhat sour when analysed, and some difficulty was experienced in properly distributing the cream. This may account for the larger error than usual.

(ii.) The fatty layer is also measured. This makes more difference than the measurement of the milk as the co-efficient of expansion, and possibly the mean variation of the density is larger than in milk. I find, however, that the temperature of the fatty layer, when measured, is about  $5^{\circ}$  above the laboratory temperature, and a maximum variation of  $10^{\circ}$  may be expected in this latter. Taking the expansion of this layer to be the same as that of butter, the maximum error would not be more than 0.8 per cent. of the fat—*i.e.*, in ordinary cases the extreme error from this cause would be less than 0.04 per cent. on the milk; actually it would be less, as the measurement of the milk would be influenced by the same cause in the same direction. The maximum variations in the density of butter-fat do not exceed 0.5 per cent. The combined extreme error from these causes would not exceed 0.05 per cent. on the milk.

(iii.) The error of measurement and graduation. As the upper and lower limits are very sharp, the volume of the fatty layer can be read with care and practice to  $\frac{1}{4}$  of a division. I find it advisable to take two or three readings as the fatty layer descends owing to the contraction of the hot liquid in the bottle, and take the mean as the correct. It is rare to find a difference in three readings.

(iv.) The variations in the composition of the fatty layer. As already stated, it consists of fat with a certain proportion of (probably) amyl (propyl, &c.) hydrogen sulphate. The exact proportion is governed by the extension of Henry's law given above. The limits of exactitude of this law, or rather the modifying circumstances, I know not. One thing is certain, however; according to this law the proportion of amyl hydrogen sulphate in the fatty layer decreases as the fatty layer increases, as the total quantity of fusel oil added is always the same. The error due to this cause, however, will always be small, as the volume of the fatty layer is very small compared to the total volume, and it may be neglected as it falls within the limits of reading. Lactic acid may be a possible source of error, as it is soluble in fat, and in a very sour milk it may make a small difference. As lactic acid is also soluble in water, and mixtures of acid and water, the error is not likely to be appreciable. It must not be forgotten, also, that the reaction of sulphuric acid on the milk may give rise to compounds soluble in fat.

(v.) The error due to the variations in the proportions used, and in the size of bottles. The variations due to length of time in whirling, and the speed of rotation. These errors may be reduced to a minimum by adhering rigidly to the same proportions. I have not yet had an opportunity of studying the influence of varying any of these, but will do so, and discuss the results in Part II. of this paper.

The total error due to all these causes will not exceed 0.1 per cent. with ordinary care. A method arriving at this exactitude deserves to be considered as more than a rough method; it becomes a reliable one.

The advantages of the method are many: It is extremely rapid, two samples can be comfortably analysed in five minutes, with reliable results. I can recommend it to public

analysts to sort out milk samples which may be sent them. The trouble of making a fat estimation by this method is very little if any more trouble than weighing out the milk, &c., for the determination of total solids. By the determination of the density, also, the solids-not-fat can be estimated by the formula of *Hehner* and myself (*THE ANALYST*, xiii., 32), or the milk scale (*THE ANALYST*, xiii., 65), with sufficient exactitude to decide whether the milk is, undoubtedly, genuine or suspicious. A great advantage is obtained by this method as the necessary further determinations can at once be proceeded with while the milk is fresh.

For commercial purposes it is also sufficient; the cost of re-agents is small, and the use of ether, with its objections, is avoided.

For dairy-control purposes it is very useful. It does not, however, fulfil all the requisites of a perfect dairy method; it is essentially a laboratory method. The facts that the reagents used, sulphuric acid and the fusel mixture, are corrosive; the attention to detail necessary—a point not likely to be appreciated by anyone, except he be a chemist; the fragile nature of the essential parts of the apparatus; and, last though far from least, the exothermic reaction—all militate strongly against the use of this apparatus in the dairy. It does not supply the widely-felt need of a universal method; in its proper sphere—the laboratory—I anticipate a future for it.

In Part II. of this paper I propose to consider the analysis of cream by this method, and to study more deeply the laws that govern the process; also, the errors and means of reducing them to a minimum.

In the absence of the author, Dr. Dyer read the following :

#### SUPPLEMENTARY NOTES ON "A NEW AND RAPID METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC BODIES."

BY W. F. KEATING STOCK, F.C.S., F.I.C.

In a communication read before the May meeting of the Society of Public Analysts (*see THE ANALYST*, June, 1892, page 109), I pointed out that the nitrogen of certain organic bodies, of which a list was given, could be rapidly converted into ammonia by treatment with manganese dioxide in presence of strong sulphuric acid. I was not present at the meeting, and as the direction of the discussion was distinctly adverse to the method I proposed I feel that it is due to the members who were present on that occasion that I should take the earliest opportunity of showing them that the method is far from being an unimportant one.

A good deal was said about the danger of the ammonia formed being acted upon by the manganese dioxide. Now it will be found on reference to the paper, that in my experiments the relation of manganese dioxide to nitrogen present ranged from 141 to 1 to 66 to 1. Also that the exposure of the substance to the action of the dioxide was not a "time" exposure—that is, the reaction was allowed to proceed until green coloration of the mass ensued without respect to time. And yet the results agreed most perfectly. I

imagined that these considerations were quite sufficient in themselves to dispose of any fear on this point.

It appeared, too, that my not giving details of analyses of pure ammonium salts was considered an important omission, but this was certainly far from what I intended. I meant to show that my method would deal perfectly with *Nitrogen in organic combination*. I said so at the outset, and consistently stuck to my text. But believing that facts are of greater value than argument, I beg to quote the following experiments as further evidence that ammonia is not lost in the "rapid" process:—

*Analysis of Ammonium Chloride.*

0.4922 grm. taken. Nitrogen calculated, 0.1288 grm. Nitrogen found, 0.1276 grm.

*Analysis of Ammonium Oxalate.*

0.4934 grm. taken. Nitrogen calculated, 0.0973 grm. Nitrogen found, .0965 grm.

It was stated during the discussion that I had admitted having entirely failed with ferrocyanide. What I said was that "attempts had been made—but so far without success." I knew when I wrote the paper where the want of success lay, and I have since corrected the error, as will, I think, be seen by the following:—

*Analysis of Potassium Ferrocyanide.*

0.5 grm. taken. Nitrogen calculated, 0.0994 grm. Nitrogen found, 0.0996 grm.

|     |   |   |   |        |   |   |   |        |   |
|-----|---|---|---|--------|---|---|---|--------|---|
| 0.5 | " | " | " | 0.0994 | " | " | " | 0.0996 | " |
|-----|---|---|---|--------|---|---|---|--------|---|

|     |   |   |   |        |   |   |   |        |   |
|-----|---|---|---|--------|---|---|---|--------|---|
| 0.5 | " | " | " | 0.0994 | " | " | " | 0.0988 | " |
|-----|---|---|---|--------|---|---|---|--------|---|

To the statement made that the analyses of uric acid are not in close agreement I hardly think it necessary to reply. A difference of 0.19 per cent. is mild as compared with what one sometimes sees in the data from which the formula of a substance is calculated; and, speaking as an analyst of long experience, I should be glad if I could always get within two-tenths of a per cent. of "the constituent sought."

These, then, were the points in the discussion which seemed to necessitate some further notice at my hands, but I should like to add that analysts have few "universal" processes, and I do not ask the members of this Society to look upon the method of procedure which I have had the honour of laying before them as universally applicable. What I do claim for it is, that with many substances the time needed for oxidation is shortened to 3 or 4 minutes; that it does away with special flasks, ordinary beakers may be used, and this greatly facilitates the work; that it dispenses with the use of mercury and consequently of potassium sulphide; that there is no need for zinc in the distillation and that fracture of the distilling flask is impossible; and, finally, that when thoroughly understood, it is capable of very wide application, yielding results which are perfectly satisfactory. I am myself using the process regularly with a degree of ease, accuracy and speed that I never expected to attain in the determination of nitrogen.

This terminated the Society's proceedings.

**The Analysis of Substitutes for Coffee.** Moscheles and R. Stelzer. (*Chem. Zeit.* 1892, xvi. 281, 282.)—The property which most readily distinguishes coffee substitutes from genuine coffee is usually their freedom from caffeine. Some such substances have been found to contain the bitter principle of the lupin as a substitute for caffeine—a most reprehensible addition. Quite recently a coffee surrogate was examined by the authors which contained powdered kola nut, which is known to contain caffeine. In distinguishing analytically between coffee and its substitutes the determination of the percentage of fat and of total extractive matter is of value. The amount of fat in coffee varies between 7 and 16 per cent., while in the factitious article it is considerably lower, namely, from 0 to 8%. The total extract from coffee is about 20-30%, while that of coffee substitutes usually varies from 50-75%. The process of analysis is hampered by the difficulty of obtaining a clear solution of the total soluble matter in the coffee, and at the same time making certain of thorough extraction. The filtration of such a solution is difficult, and it commonly becomes turbid on cooling, from the precipitation of gum, dextrin, and similar bodies. The authors have, in consequence, abandoned the attempt to obtain perfect extraction, the more readily because it does not represent what takes place in the actual use of coffee. Their practice is to powder finely 25-30 grms. of the substance and digest it for half-an-hour on the water-bath with 500 c.c. of water. The solution is made up to one litre, allowed to cool and a portion drawn off and evaporated to dryness, with the addition of a weighed quantity of ignited sand, to constant weight. This represents the extract obtained under ordinary domestic conditions. The following results were obtained with some modern coffee surrogates :—

| CHICORY MALT COFFEE FROM R. BAER, BERLIN. |     |     |     |     |                         |       |                                 |                         |
|---|-----|-----|-----|-----|-------------------------|-------|---------------------------------|-------------------------|
| Extract                                   | ... | ... | ... | ... | ...                     | ...   | ...                             | 36.00%                  |
| Moisture                                  | ... | ... | ... | ... | ...                     | ...   | ...                             | 2.65                    |
| Woody fibre                               | ... | ... | ... | ... | ...                     | ...   | ...                             | 12.93                   |
| Natural ash                               | ... | ... | ... | ... | ...                     | ...   | ...                             | 2.11                    |
| Sand                                      | ... | ... | ... | ... | ...                     | ...   | ...                             | 0.05                    |
| Soluble proteids                          | ... | ... | ... | ... | ...                     | ...   | ...                             | 0.25                    |
| Gum and dextrin                           | ... | ... | ... | ... | ...                     | ...   | ...                             | 24.14                   |
| Sugar...                                  | ... | ... | ... | ... | ...                     | ...   | ...                             | 4.90                    |
| Starch, etc.                              | ... | ... | ... | ... | ...                     | ...   | ...                             | 42.13                   |
| Fat                                       | ... | ... | ... | ... | ...                     | ...   | ...                             | 1.84                    |
| Caffein                                   | ... | ... | ... | ... | ...                     | ...   | ...                             | —                       |
|   |     |     |     |     |                         |       |                                 |                         |
| Linde.                                    |     |     |     |     | Linde Bros.'<br>Coffee. |       | Linde Bros.'<br>Coffee Essence. | Feine's Malt<br>Coffee. |
| Extract                                   | ... | ... | ... | ... | ...                     | 68.14 | 72.03                           | 60.33                   |
| Soluble proteids                          | ... | ... | ... | ... | ...                     | 4.61  | 4.56                            | 7.56                    |
| Sugar and dextrin                         | ... | ... | ... | ... | ...                     | 59.38 | 59.53                           | 59.37                   |
| Other extractive substances               | ... | ... | ... | ... | ...                     | 35.81 | 35.81                           | 33.07                   |
| Moisture                                  | ... | ... | ... | ... | ...                     | 4.63  | 3.23                            | 2.13                    |
| Ash                                       | ... | ... | ... | ... | ...                     | 5.03  | 2.35                            | 1.87                    |



## COFFEE SUBSTITUTE OF UNKNOWN ORIGIN.

|                                     |     |     |     |     |     |     |        |
|-------------------------------------|-----|-----|-----|-----|-----|-----|--------|
| Extract ...                         | ... | ... | ... | ... | ... | ... | 46.52% |
| Soluble proteids                    | ... | ... | ... | ... | ... | ... | 13.94  |
| Nitrogenous extractive material     | ... | ... | ... | ... | ... | ... | 5.18   |
| Non-nitrogenous extractive material | ... | ... | ... | ... | ... | ... | 18.88  |
| Sugar ...                           | ... | ... | ... | ... | ... | ... | 12.00  |
| Soluble salts                       | ... | ... | ... | ... | ... | ... | 2.32   |
| Moisture                            | ... | ... | ... | ... | ... | ... | 8.01   |
| Fat ...                             | ... | ... | ... | ... | ... | ... | 4.27   |
| Woody fibre                         | ... | ... | ... | ... | ... | ... | 22.04  |
| Natural ash                         | ... | ... | ... | ... | ... | ... | 0.74   |
| Sand ...                            | ... | ... | ... | ... | ... | ... | 0.48   |
| Caffein ...                         | ... | ... | ... | ... | ... | ... | 0.31   |

In all cases the proteid and extractive substances given above are those in the "extract" which was obtained by the method already described, no attempt at complete extraction being made.

B. B.

**The Determination of Crude Fibre.** S. Gabel. (*Zeits. Physiol. Chem.*, 1892, xvi., 370, through *Chem. Zeit.*)—The author has examined Hönig's method for the determination of crude fibre and starch. The method in question depends upon the fact that albumen and starch become soluble in water, after heating with glycerine to 210° C, while cellulose is not attacked. As the process was employed by the author solely for the determination of crude fibre, the whole of the operations for the separation of the starch could be omitted. In place of the sulphuric acid bath, used by Hönig, the author found that a naked flame could be more conveniently employed, as regulation of the temperature was thereby rendered easier. Certain modifications were necessary, on account of the nitrogenous and non-nitrogenous substances, other than cellulose, being unattacked by glycerine alone. The requisite additional activity of the attacking reagent can be obtained by the use of a caustic alkali, and the method thus modified, is carried out as follows:—2 grms. of the substance are heated, in a 250 c.c. flask, on a piece of wire netting, over a naked flame, with 60 c.c. of a solution of caustic alkali in glycerine, containing 33 grms. of caustic potash per litre. A vigorous reaction sets in usually at about 130° C, at which point precaution is necessary to moderate the foaming that takes place. At a temperature of 160° C, the reaction is for the most part finished, after which the temperature is gradually raised to 180° C. The product is then emptied into a dish containing 200 c.c. of boiling water, well stirred, allowed to settle thoroughly, and the supernatant liquor drawn off with a syphon, having a piece of linen tied over the end. The residue is then boiled up again with 200 c.c. of water, and a third time with the same quantity of water, to which has been added 5 c.c. of 25 per cent., hydrochloric acid. The unattacked crude fibre is washed with alcohol and ether, as in the Wendee method. The extremely small quantity of nitrogenous substances left in the crude fibre appears to be, in most cases, negligible.

B. B.

**A Simple Method for the Detection of Frozen Meat. Maljean.** (*J. Pharm. Chim.*, 1892, xxv. 348, through *Chem. Zeit.*)—The process adopted by the author for distinguishing between fresh meat and that which has been preserved in the frozen state, consists in expressing a little blood or meat juice from the sample, and examining it under the microscope. The whole operation must be performed quickly, in order to prevent any drying up of the liquid under examination. When the juice of fresh flesh is thus examined, it is seen to contain numerous red corpuscles, which are normal in colour, and float in a clear serum. In the case of blood from frozen flesh, the corpuscles have dissolved in the serum under the influence of the low temperature, and not a single normal red corpuscle can be seen. The hemoglobin escapes into the serum, and appears as irregular, yellow-brown crystals. These may be frequently seen by the naked eye, but, in every case, can be readily detected under the microscope. B. B.

**The Determination of Glycerine in Wine. M. T. Lecco.** (*Chem. Zeit.*, 1892, xvi., 504.)—The usual method of determining glycerine in wine is that officially recognised by the Berlin Committee of 1884, although it is far from ideal. The residue which is obtained by evaporating the wine together with quartz sand and milk of lime nearly to dryness, is difficult to remove from the dish in which the evaporation has been performed, and a certain quantity of glycerine is apt to be left in the residue after extraction. The following are the modifications proposed by the author:—10 c.c. of the wine are well mixed with 0.1 of a grm. of powdered calcium hydrate, 10 grms. of quartz sand added, and the whole evaporated almost to dryness on the water bath. The residue is extracted four or five times with hot absolute alcohol, and the extract, amounting to 40—50 c.c., is filtered into a flask holding about 100 c.c., then evaporated on the water bath the syrupy residue dissolved in 5 c.c. of alcohol, 7.5 c.c. of ether added, the flask well corked, allowed to stand some hours, and the clear solution poured into a weighed flask (previously filtering if necessary), the alcoholic liquid evaporated off, and the residue dried for one hour in the water oven and weighed. This method, when tried on seven samples of Servian wine, containing from 0.7 to 1.0 per cent. of glycerine, gave results ranging from 0.1 to 0.36 per cent. higher than the old method; while, at the same time, closely concordant results were obtained by repetitions of the new method, and also when it was carried out on a scale ten times as great as that prescribed above. In order to ascertain whether the compound formed of lime and glycerine by evaporation to complete dryness resisted the solvent action of the alcohol, further experiments were made in which this condition obtained, with the result that the percentage of glycerine found was not diminished, but slightly increased. Should this observation be confirmed, the need for special precaution in the evaporation will be obviated. The author also states that he has obtained good results by evaporating an aliquot portion of the alcoholic extract, by which means previous filtration and washing necessary to the original process are avoided. He has yet to prove the purity of the glycerine thus isolated. B. B.

## LEGAL.

## SALE OF COFFEE AND CHICORY.

JONES *v.* THE VESTRY OF BERMONDSEY.

An appeal case, arising out of the judgment delivered by Mr. Slade in a case of the sale of a mixture of coffee and chicory, was heard before Sir Peter Edlin, Q.C., on June the 15th, 1892. The case as stated by Mr. Slade was as follows:—

“In this case the prosecutor entered the shop of the defendant, a grocer, and asked for a quarter of a pound of coffee. The assistant inquired, ‘A quarter of a pound of shilling?’ He said, ‘Yes,’ and was served with a mixture in a brown paper parcel, for which he paid 3d. On analysis the mixture was found to contain 40 per cent. of coffee and 60 per cent. of chicory. On the outside of the wrapper were legibly printed these words: ‘This is sold as a mixture of chicory and coffee.’ This was admitted to be a sufficient protection to the vendor under the Food and Drugs Act, unless it could be shown there was a fraudulent intent under the 8th section of the Act. It was proved before me that the cost of pure coffee is 1s. 4d. per lb., and of chicory 4d. per lb., so that the mixture cost the vendor about 9½d. per lb., which he retailed to the customer at 1s. per lb. So it comes to this—first, the article asked for is not supplied; second, the shop-keeper cannot be punished since he protects himself by a label, unless fraud is proved; and third, the customer is not prejudiced financially because he gets his money’s worth. It appears that coffee is generally mixed with chicory, and that pure coffee (like pure mustard) is hardly known as an article of domestic use; and it is legal to sell a mixture if proper precaution is taken. But here the 8th section of the Act steps in, which says that nothing shall be added which is intended fraudulently to increase its bulk, weight, or measure, or conceal its inferior quality.’ And why? Because a customer is entitled to get the article which he asked for. The mere use of the label opens the door to fraud. It is very difficult to draw the line as to the proportion of the ingredient. I am aware of the cases of *Lydiard v. Reece*, *Horder v. Meddings*, and *Horder v. Adams*. These cases seem to show that fraud is purely a question of fact for the magistrates to decide. After much deliberation I have come to the conclusion that the presence of a larger proportion of the inferior ingredient as disclosed in this case (though not excessive) is sufficient to bring it within the mischief aimed at by the 8th section of the Act, and that to hold otherwise would render nugatory the provision which was passed for the protection of the poorer classes. The defendant will be fined £3, and will have to pay 12s. 6d. costs.”

After the case had been argued at considerable length (two days) before Sir Peter Edlin, the following judgment was delivered :—

“ I have arrived at the conclusion that this conviction should be upheld. I would in the first place refer to what has been recorded as inaccuracy in the conviction, which describes this as an article of drink. It may be more properly described as an article of food. It would not become drink until water is mixed with it. Therefore the word ‘drink’ which occurs twice in this conviction must be altered to ‘food.’ Let it be understood that this correction is made. Now with regard to the judgment of the learned magistrate, Mr. Wyndham Slade. In substance I agree with it; I agree with him in the conclusion at which he arrives after an obviously very careful consideration of the facts as they were laid before him. We here have had the advantage of hearing other witnesses, and, if I am not mistaken, more witnesses than were called before Mr. Slade; but I do not think that what they have stated could have materially altered the facts as they were disclosed before the learned magistrate. I must say I am unable to follow him, for judging from what appears in this copy of his judgment he says that this sale was not prejudicial financially to Mr. Toogood. It seems to me that, from the very nature of the mixture that was sold to him, he would be prejudiced, as it would seem from what he has himself admitted that when he accepted the mixture, having asked for coffee, he was not aware of the proportion of the two ingredients—chicory and coffee. He did not know there was an undue proportion, namely, 60 per cent. of chicory and only 40 per cent. of coffee. We have it proved before us, and it cannot be denied, that even if this mixture had been equal in the proportions, that is to say, the same amount of coffee as there was of chicory, the profit to Mr. Jones would be 2d. in the 1s. And we have it proved, moreover, that for coffee when sold, the cheapest coffee that is retailed, the profit is only 2d. in 1s. 6d., and that chicory when sold realised a profit of 2d. in respect of 6d. So that it is obvious when we have regard to the disproportion shown here—the much larger proportion of chicory to coffee in the mixture actually sold—that it is distinctly to the prejudice of the buyer that he should purchase that mixture instead of having an equal weight of two several ingredients, of which the article is composed. Then we have to consider what were those proportions—what we may fairly consider were those proportions, and what probable profit they would bring to the seller; and we find that upon a shillingworth it would bring to him a profit of 3d. and some four-fifths of a farthing. Without going into the fractions we may say there was a clear profit of 25 per cent., whereas if the two articles were sold separately the profit would be only 4d. in 2s., or one-sixth. Now, having regard to the great disproportion in the value of the several ingredients, it seems to me to be the duty of the seller to take care—if I may say so, extra care—if he sells, as he lawfully may do, a mixture of chicory and coffee, to disclose to his buyer that it is a mixture. It is incumbent upon him also to take care that the mixture is in due proportions, and that there is not that excess of the cheaper article which, having regard to the price, would operate prejudicially to the purchaser of the coffee. Then we have to ask ourselves upon

the facts before us whether the appellant has brought himself in this transaction within the saving provision of the 8th section of the Act. I should be loth to say I could come to a conclusion that there had been an intention of fraud, but I do think that sufficient has been shown in this case to disentitle him to say that there was not that fraudulent admixture—that the mixture was not of such inferior quality as entitles him to the benefit of this saving clause of the 8th section of the Act of Parliament. I think, therefore, that Mr. Slade was right in his conclusion that this was a sale to the prejudice of the buyer. Now Mr. Slade's expressions are deserving of notice. They indicate the care which he had bestowed upon the case, and I may endorse it as a substantially correct view of what I take in this case. He said: 'After much deliberation I have come to the conclusion that the presence of the larger proportion of the inferior ingredient as disclosed in this case (though not excessive) is sufficient to bring it within the scope of the 8th section.' I concur in that expression, and I agree also with him in holding that 'otherwise it would render nugatory the provision which was passed for the protection of the poorer classes.' This provision was passed for the protection of the buyer, and if the seller is desirous of availing himself of the provision in the 8th section, he must be careful to do so in such a way as gives full notice to the purchaser of what he is buying; and he must be careful also that he is not so compounding the ingredients as to constitute it an article of inferior quality to that which he is professing to sell. I cannot think that the expression of the words of the label, 'A mixture of chicory and coffee,' would indicate to any purchaser that the mixture was in an undue proportion of 60 per cent. of the cheaper article—the much cheaper article—and only 40 per cent. of coffee as in this case. For these reasons I think the magistrate came to a right conclusion, and I must confirm this conviction."

Defendant's counsel asked his lordship to state a case for the Court of Queen's Bench. Sir Peter at first declined, as he was doubtful whether the High Court would entertain the case; but upon being pressed, he promised to further consider the matter with a view to presenting the case in such a manner to the judges, that there would be some probability of their entertaining it.

### SAMPLES OF MILK TAKEN FOR ANALYSIS.

ROLPH *v.* THOMPSON.

On February the 27th, 1892, an inspector under the Food and Drugs Act intercepted six churns of milk consigned to a London milk dealer, which had arrived at King's Cross station from the country. He took a sample from each churn, and divided it into two parts; one portion he forwarded to the Public Analyst, the other he retained himself. Prosecutions for adulteration were instituted in each case, and dismissed by the magistrate on the ground that the samples should have been delivered whole to the analyst, the division of the samples constituting an irregularity. An appeal was carried to the Court of Queen's Bench, and heard on June 16th, when Mr. Justice Grantham and Mr. Justice Charles expressed the opinion that the magistrate's decision was wrong and that the fact

of the inspector dividing the samples did not affect the proper delivery to the analyst. The case was therefore remitted back to the magistrate.

### REVIEW.

FARM-YARD MANURE: Its Nature, Composition and Treatment. By C. M. AIKMAN, M.A., B.Sc., F.R.S.E. (Wm. Blackwood and Sons, Edinburgh and London.) 1s. 6d.

THIS is really a section, published in advance, of a large work on "Soils and Manures," on which the author is still engaged. The little volume now under notice gives evidence of thorough literary labour, and augurs well for the value of the complete work, of which it forms the first instalment. While freely acknowledging his indebtedness to the authors of existing manuals of agriculture and agricultural chemistry, Mr. Aikman has evidently spent pains, by the study of contemporary work, in bringing his monograph up to date. In these days of cheap artificial manures and cheap food, farmyard manure is, perhaps, a less vital subject of interest to the farmer than it used to be. "Muck" will always have its special functions—those affecting the very important physical features of the soil—which can, perhaps, be performed by no other agent. But its quality, in the sense of its actual chemical fertilising strength, is of less importance than in the days that preceded cheap nitrate of soda and abundant artificial phosphates. We do not suggest that sensible farmers would take less pains now than formerly, to preserve the full value of the manure-heap, but that probably fewer advanced farmers find it worth while to take the thought that they would once have taken in order to enrich it. With nitrate of soda at 8s. 6d. per cwt., it would scarcely pay to use a more expensive nitrogenous food to fatten stock in place of a cheaper farinaceous one, *merely* for the sake of strengthening the "dung." Nevertheless, if the chemistry of farm-yard manure has not at the moment the full economical importance that it once had, it is, at the same time, desirable that every farmer should have some knowledge of its principles, and indispensable that the real student of the science of agriculture should have a clear insight into them. This little book will be found interesting, either to the light or to the careful reader, and, to study the convenience of both, Mr. Aikman has separated most of his tabular and statistical matter from the general context, and placed it in an appendix. The small price at which the book is published should lead to its taking a place, in advance of the larger work that we are promised, on the shelf devoted to agricultural text-books in every library where such a shelf exists.

### APPOINTMENT.

Mr. Arthur E. Ekins, F.C.S., of St. Albans, has been appointed by the Herts County Council public analyst for Hertfordshire, exclusive of the city of St. Albans.

# THE ANALYST.

SEPTEMBER, 1892.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

### NOTES FROM THE KHEDIVIAL LABORATORY.

*Read at Meeting, June 1st, 1892.*

By H. DROOP RICHMOND (late Second Chemist to the Egyptian Government).

**7. On a Sample of Milk yielded by an Arab Woman.**—Although the analysis of isolated samples of milk cannot be accepted as giving much definite information, still I think that it may not be without interest to record the analysis of a sample of milk yielded by an Arab woman. It was one of two samples sent by a medical man for the purpose of judging which would be most suitable for an infant. As far as I can find, no milk of Arab women has been analysed, and it is still an open question as to whether race has any influence on the composition of milk in the human subject as it has in the cow. Probably, personal differences have much more influence; and I therefore record the analysis without further comment:—

|                       |     |     |     |     |             |
|-----------------------|-----|-----|-----|-----|-------------|
| Water                 | ... | ... | ... | ... | 85.92       |
| Fat                   | ... | ... | ... | ... | 5.31        |
| Sugar                 | ... | ... | ... | ... | 6.41        |
| Proteids*             | ... | ... | ... | ... | 2.16        |
| Ash                   | ... | ... | ... | ... | .20         |
|                       |     |     |     |     | <hr/>       |
|                       |     |     |     |     | 100.00      |
| * Containing Nitrogen |     |     |     |     | ... .. .339 |

**8. Egyptian Flour.**—As, as far as I can find, no analyses of Egyptian flour have been published, the following may be of interest. It is considered a very inferior flour, and although imported in fair quantities into England, is not used for bread-making, but rather for the manufacture of starch.

It is very rare to find Egyptian flours which, on microscopic examination, do not show the presence of a leguminous starch, and also often of "doura" or maize; probably, the presence of "doura" is as frequent as that of the leguminous starch; but it is difficult to detect in small quantities, it resembling very much the wheat starch, but giving a much

more distinct cross in water when examined by polarised light. These foreign starches, in such small quantities as to preclude the idea of adulteration, I have found in samples which have come from sources which almost entirely exclude suspicion, and their presence is due to the fact that very little care is taken to prevent the accidental occurrence of the foreign starches, wheat being ground in the same mill in which "doura" or "fool" (beans) have been previously ground, with only a superficial cleaning. It is also of not unusual occurrence to find husk in considerable quantities and dirt.

The only method of analysis which needs discussion is the estimation of the soluble constituents. Ten grammes of the flour are shaken with 250 c.c. of water at 15° for an hour, the temperature being kept as constant as possible, and then allowed to stand four hours, at the expiration of which the solution is filtered, and in it are estimated the total solids, ash, nitrogen, nitrogen in tannin precipitate, and acidity as lactic acid. The following figures have been established:—

For the total solids in good flours, from 5 to 6 per cent., going up to nearly 10 per cent. in inferior samples.

The ash is about 10 per cent. of the total solids, being slightly less in good samples and more in bad.

The total soluble nitrogen, and that in the tannin precipitate, are practically the same in good samples, while in inferior ones there is a difference of nearly .1 per cent.

The character of the tannin precipitate differs in good and bad samples, being in good ones whiter and more voluminous than in bad ones, in which it takes a brownish pink hue.

The following figures were obtained in four typical samples:—

|                         |     |     |     | Good.  | Moderate. | Bad A. | Bad B. |
|-------------------------|-----|-----|-----|--------|-----------|--------|--------|
| Moisture                | ... | ... | ... | 11.63  | 11.70     | 8.35   | 9.50   |
| Ash                     | ... | ... | ... | .65    | 1.72      | 1.80   | 1.92   |
| Gluten                  | ... | ... | ... | 7.61   | 7.58      | 8.21   | 8.06   |
| Soluble Albuminoids...  |     |     | ... | 1.28   | 1.56      | 1.39   | 1.41   |
| Non-Albuminoids         | ... | ... |     | Trace  | .10       | .17    | .24    |
| Cellulose               | ... | ... | ... | .44    | .49       | .63    | .59    |
| Starch (difference)     | ... | ... | ... | 72.05  | 67.57     | 70.96  | 70.04  |
| Amylan, Sugar, &c.      | ... | ... | ... | 4.16   | 6.14      | 6.04   | 6.50   |
| Fat                     | ... | ... | ... | 2.18   | 3.14      | 2.45   | 1.74   |
|                         |     |     |     | 100.00 | 100.00    | 100.00 | 100.00 |
| Soluble in Water        | ..  | ... | ... | 5.88   | 8.68      | 8.58   | 9.12   |
| Ash                     | ... | ... | ... | .44    | .88       | .97    | .97    |
| Nitrogen                | ... | ... | ... | .205   | .283      | .278   | .305   |
| Nitrogen in Tannin ppt. | ... | ... | ... | .203   | .250      | .222   | .225   |
| Total Nitrogen          | ... | ... | ... | 1.423  | 1.500     | 1.591  | 1.584  |
| Phosphoric Acid in Ash  | ... | ... | ... | .27    | .60       | .56    | .81    |



**9. Some Egyptian Waters.**—The great source of water in Egypt is the Nile, and of the water of the Nile I shall speak at another time; in this note I propose only to touch on a few waters not directly connected with the Nile.

The waters I have to speak of can be divided into two classes, (*a*) those probably having filtered from the Nile through a considerable distance, and (*b*) those probably having no connection with the Nile.

In order to compare these I give the average (mineral) composition of the Nile water :—

|  |     |     |     |                             |
|--|-----|-----|-----|-----------------------------|
| Silica, Fe <sub>2</sub> O <sub>3</sub> , &c. | ... | ... | ... | ·976                        |
| Lime   | ... | ... | ... | 4·218                       |
| Magnesia                                     | ... | ... | ... | 1·005                       |
| Potash                                       | ... | ... | ... | 1·437                       |
| Soda   | ... | ... | ... | ·584                        |
| Chlorine                                     | ... | ... | ... | ·755                        |
| Sulphuric Acid                               | ... | ... | ... | 2·170                       |
| Carbonic Acid                                | ... | ... | ... | 3·843                       |
| Nitric and Phosphoric Acid                   | ... | ... | ... | None, or very faint traces. |
|  |     |     |     | <hr/> 14·988                |
| Less O=Cl                                    | ... | ... | ... | ·170                        |
|  |     |     |     | 14·818                      |

The two first waters of which I wish to speak come from near Cairo. The first is a shallow well water in Cairo, about a mile and a-half from the Nile, in the Ezbekieh quarter, and may be taken as a typical one; the second is from a deep boring at Mena House Hotel, under the shadow of the Great Pyramid, about 8 miles from Cairo and 6 miles from the Nile. Both are remarkable for their great organic purity and the considerable amount (in Egypt) of nitrates; indeed, the water of the Mena House Hotel is the purest I have ever examined.

The analysis is as follows :—

|                         | No. 1. | No. 2. |
|-------------------------|--------|--------|
| Free Ammonia            | ·013   | None   |
| Albuminoid Ammonia      | ·005   | None   |
| Oxygen absorbed 15 min. | ·021   | ·003   |
| „ „ 4 hours             | ·057   | ·053   |
| Total Solids            | 101·28 | 25·96  |
| Loss on Ignition        | 8·32   | ·60    |
| Silica                  | 4·68   | 2·83   |
| Oxide of Iron, &c.      | ·40    | ·30    |
| Lime                    | 12·30  | 6·27   |
| Magnesia                | 7·99   | 2·38   |

|                      |     |     |     |              |             |
|----------------------|-----|-----|-----|--------------|-------------|
| Potash               | ... | ... | ... | 11.35        | .61         |
| Soda                 | ... | ... | ... | 18.49        | 2.48        |
| Chlorine             | ... | ... | ... | 8.91         | 2.53        |
| Nitric Acid          | ... | ... | ... | .73          | .65         |
| Sulphuric Acid       | ... | ... | ... | 17.40        | .95         |
| Carbonic             | „   | ... | ..  | 21.72        | 7.22        |
|                      |     |     |     | 103.97       | 26.23       |
| Less Oxygen=Chlorine |     |     |     | 2.01         | .57         |
|                      |     |     |     | <hr/> 101.96 | <hr/> 25.66 |

The first water has evidently taken up considerable amounts of salts during its passage from the Nile, salts probably having their origin from the same river. The silica is very high.

The second water has taken up much less salts, and a doubt has arisen as to whether it is Nile water, for the following reasons:—It contains much less potash and sulphuric acid than the Nile, and it is difficult to see how these bodies have been lost, as it flows through a country almost devoid of vegetation. It is below the level of the Nile, and its rise and fall does not coincide with that of the Nile, but follows it at a considerable period and to a limited extent; unless we admit that it has travelled hundreds of miles underground, and certain other considerations render this unlikely, it can have no other source than the Nile. It comes up through limestone, and sometimes has a tendency to deposit chalk, which it takes up again on exposure to the air; the uncombined carbonic acid is very small, .88 parts per 100,000.

I am of opinion that it has no connection with the Nile at Cairo, but has its source higher up.

A third water, which may be taken as typical of the non-sulphurous waters of Helouan, 20 miles above Cairo:—

|                      |     |     |     |             |
|----------------------|-----|-----|-----|-------------|
| Silica               | ... | ... | ... | 1.8         |
| Oxide of Iron, &c.   | ... | ... | ... | 1.4         |
| Lime                 | ... | ... | ... | 60.8        |
| Magnesia             | ... | ... | ... | 57.1        |
| Potash               | ... | ... | ... | 1.4         |
| Soda                 | ... | ... | ..  | 298.0       |
| Chlorine             | ... | ... | ... | 417.4       |
| Sulphuric Acid       | ... | ... | ... | 97.5        |
| Carbonic Acid...     | ... | ... | ... | 11.0        |
|                      |     |     |     | <hr/> 946.4 |
| less Oxygen=Chlorine |     |     |     | 94.0        |

852.4

Density, 1.0067.

## THE ANALYST.

This is simply the Nile water which has taken up a quantity of the native salt, which abounds at Helouan, and calls for no remark.

The sulphurous waters of Helouan have been ably treated of by Prof. Gastinel Pasha (*Etude sur les Eaux Thermales de Helouan*).

In class (b) as typical of the saline waters which occur at Mex, Edko, Bourloss, and other places on the North of the Delta and near Suez, may be taken that of Shaloof (near Suez).

As it is very highly concentrated (having a density of 1.1939), the results are expressed as percentages, and not as parts per 100,000. It is quite saturated with salts, and agrees very closely in composition both with concentrated sea water and with other saline waters of Egypt; there is no doubt that these waters are derived from the sea, and they are the origin of the salt industry.

### No. 4.

|                          |     |     |         |                                      |     |     |        |
|--------------------------|-----|-----|---------|--------------------------------------|-----|-----|--------|
| Water                    | ... | ... | 75.660  | Water                                | ... | ... | 75.660 |
| Silica                   | ... | ... | .002    | SiO <sub>2</sub>                     | ... | ... | .002   |
| Oxide of Iron, &c.       | ... | ... | Traces  | Fe <sub>2</sub> O <sub>3</sub> , &c. | ... | ... | Traces |
| Lime                     | ... | ... | .627    | CaSO <sub>4</sub>                    | ... | ... | .163   |
| Magnesia                 | ... | ... | 1.281   | CaCl <sub>2</sub>                    | ... | ... | 1.110  |
| Potash                   | ... | ... | .120    | MgCl <sub>2</sub>                    | ... | ... | 3.024  |
| Soda                     | ... | ... | 10.497  | NaCl                                 | ... | ... | 19.808 |
| Chlorine                 | ... | ... | 15.076  | KCl                                  | ... | ... | .190   |
| Bromine                  | ... | ... | .030    | MgBr <sub>2</sub>                    | ... | ... | .034   |
| Iodine                   | ... | ... | Traces  |                                      |     |     |        |
| Sulphuric Acid           | ... | ... | .096    |                                      |     |     |        |
|                          |     |     | <hr/>   |                                      |     |     | <hr/>  |
|                          |     |     | 103.359 |                                      |     |     | 99.991 |
| Less oxygen = Cl and Br. |     |     | 3.370   |                                      |     |     |        |
|                          |     |     | <hr/>   |                                      |     |     |        |
|                          |     |     | 99.989  |                                      |     |     |        |

The next two waters occur in a cave at Bahnesa, about 10 miles to the West of Minieh, and were taken at two different times this water is about fifteen feet above the Nile, and its source, which is unknown, is probably not that river. The analyses are:—

|                    |     |     |     | No. 5. | No. 6. |
|--------------------|-----|-----|-----|--------|--------|
| Silica             | ... | ... | ... | 1.96   | 2.20   |
| Oxide of Iron, &c. | ... | ... | ..  | .64    | .20    |
| Lime               | ... | ... | ... | 21.16  | 17.81  |
| Magnesia           | ... | ... | ... | 14.98  | 15.57  |
| Potash             | ... | ... | ... | 73.08  | 77.68  |
| Soda               | ... | ... | ... | 31.07  | 29.11  |
| Sulphuric Acid     | ... | ..  | ... | 26.68  | 21.32  |

|                        |     |     |     |        |        |
|------------------------|-----|-----|-----|--------|--------|
| Chlorine               | ... | ... | ... | 122.57 | 121.37 |
| Carbonic Acid          | ... | ... | ... | none   | 1.19   |
|                        |     |     |     | 292.14 | 286.45 |
| Less Oxygen = Chlorine | ... |     |     | 27.68  | 27.45  |
|                        |     |     |     | 264.46 | 259.00 |
| Acidity as HCl         | ... | ... |     | 1.14   | None   |

These waters are remarkable; first, for the large quantity of potash they contain; second, for the fact that the first is *acid*, while the other is not; what the significance of this fact is I know not; it may indicate coal with its attendant pyrites, or possibly volcanic sulphur.

In the same district, although many miles away, occur, a water containing ferrous carbonate, which of course oxidizes and deposits, and which is used as a tonic; a purgative water containing magnesium, sodium and potassium sulphates; a water reputed to cure syphilis; and a water said to have the power of dyeing red fabrics (alizarin?) black; these last two I have not had the opportunity of examining.

Appendix. The bases are calculated with the acids as salts.

|                                     | Nile.  | No. 1. | No. 2. | No. 3. | No. 5. | No. 6. |
|-------------------------------------|--------|--------|--------|--------|--------|--------|
| Mg(NO <sub>3</sub> ) <sub>2</sub>   | —      | 1·16   | ·90    | —      | —      | —      |
| Na <sub>2</sub> SO <sub>4</sub>     | 1·337  | 30·81  | 1·68   | —      | —      | —      |
| CaSO <sub>4</sub>                   | 1·780  | —      | —      | —      | 45·10  | 36·24  |
| MgSO <sub>4</sub>                   | —      | —      | —      | 44·7   | —      | —      |
| K <sub>2</sub> SO <sub>4</sub>      | ·806   | —      | —      | 115·1  | —      | —      |
| CaCO <sub>3</sub>                   | 6·222  | 21·96  | 11·19  | 23·9   | —      | 2·70   |
| MgCO <sub>3</sub>                   | 2·110  | 15·88  | 4·43   | —      | —      | —      |
| K <sub>2</sub> CO <sub>3</sub>      | —      | 11·75  | —      | —      | —      | —      |
| NaCl                                | —      | 9·98   | 3·27   | 562·4  | 58·63  | 54·93  |
| KCl                                 | 1·587  | 5·34   | ·97    | 2·2    | 115·75 | 123·03 |
| CaCl <sub>2</sub>                   | —      | —      | —      | —      | 5·43   | 2·73   |
| MgCl <sub>2</sub>                   | —      | —      | ·09    | 100·4  | 35·58  | 36·97  |
| (FeAl) <sub>2</sub> Cl <sub>3</sub> | —      | —      | —      | —      | ·90    | —      |
| HCl                                 | —      | —      | —      | —      | 1·14   | —      |
| Fe <sub>2</sub> O <sub>3</sub> }    | ·976 { | ·40    | ·30    | 1·4    | —      | ·20    |
| SiO <sub>2</sub> }                  |        | 4·68   | 2·83   | 1·8    | 1·96   | 2·20   |
|                                     | 14·818 | 101·96 | 25·66  | 851·9  | 264·49 | 259·00 |

**10.—Normal Sulphuric Acid, Barium Sulphate, and Decinormal Barium Hydrate.**—An approximately normal solution of sulphuric acid was prepared by mixing

90 c.c. of freshly distilled sulphuric acid and three litres of distilled water. As this solution was to serve as the standard volumetric solution, it was standardized with great care.

The density was taken at 15°, 20°, 25° and 30°, with the following results:—

| Temp. T. |     |     |     | Density = $D \frac{T}{4^{\circ}}$                                 |
|----------|-----|-----|-----|---|
| 15°      | ... | ... | ... | $\left\{ \begin{array}{l} 1.03355 \\ 1.03356 \end{array} \right.$ |
| 20°      | ... | ... | ... | 1.03200   |
| 25°      | ... | ... | ... | 1.03025   |
| 30°      | ... | ... | ... | 1.02835   |

From the table given by Pickering (*Jour. Chem. Soc.*), the strength of the solution was calculated

|                     |     |     |     |                           |
|---------------------|-----|-----|-----|---------------------------|
| from results at 15° | ... | ... | ... | 5.062 per cent. $H_2SO_4$ |
| „ „ 20°             | ... | ... | ... | 5.061 „ „                 |
| „ „ 25°             | ... | ... | ... | 5.050 „ „                 |
| „ „ 30°             | ... | ... | ... | 5.033 „ „                 |
| Mean                | ... | ... | ... | <hr/> 5.051 „ „           |

Correcting those of Pickering's results which stood nearest to my determinations, the density at 15° corresponded to a strength of 5.071 per cent.  $H_2SO_4$ .

Three gravimetric determinations as barium sulphate, using from six to nine grams of the solution gave

5.102 per cent.  
5.105 „  
5.104 „

Mean ... 5.104 per cent.  $H_2SO_4$

The formula calculated for the strength of the solution from my results is:—

Strength at  $T^{\circ}$  = Strength at 15°  $[1.0000 - 0.0003 (T - 15^{\circ}) - 0.0000022 (T - 15^{\circ})^2]$

This formula is probably not strictly exact, but its error is within the limits of titration.

1 c.c. of my normal solution =  $0.0431 - 0.000013 (T - 15^{\circ}) - 0.000000094 (T - 15^{\circ})^2$  grs.  $SO_3$ .

Weighed quantities were, however, generally used.

Experiments of the estimation of sulphuric acid and barium as barium sulphate were carried out. As this is not new, I shall not give them in detail; but as it is highly desirable from time to time to emphasize the precautions necessary to be observed in this most important determination, I give the conclusions:—

(i.) The solution must contain free hydrochloric acid in the proportion of at least 3 HCl to 1  $\text{SO}_3$ .

(ii.) An excess of barium chloride must be avoided, and especially crystals of barium chloride must not be used.

(iii.) The solution must be gently boiling, and the precipitant added gradually. I found it best to add a solution of barium chloride (10 per cent.) drop by drop from a pipette to a gently boiling solution, until precipitation seemed complete, to continue boiling gently for ten minutes, to allow to settle, and test with another drop.

(iv.) After precipitation, at least an hour or two's repose is necessary; if the solution is very acid or if the quantity is very small, twenty-four hours, standing should be given.

(v.) The presence of iron, aluminium, and alkaline salts, except in traces, and of nitrates, should be avoided.

(vi.) If ignited slowly at first, and then strongly in a current of air, the precipitate may be burnt with the filter paper.

With these precautions, I believe this determination to be one of the most exact existing. Duplicates need not differ by more than half a milligram.

An approximately decinormal solution of barium hydrate was prepared with three-times-crystallized barium hydrate.

It was titrated with the normal sulphuric acid.

(i.) 3.9152 grs. normal sulphuric acid (5.104 per cent.) = 40.78 c.c.  $\frac{N}{10}$  took 39.48 c.c. barium hydrate solution; this gave on evaporation and ignition 0.4791 grs.  $\text{BaSO}_4$ , and the same after ignition with sulphuric acid.

(ii.) 2.9278 grs. N. sulphuric acid solution (5.104 per cent.) = 30.50 c.c.  $\frac{N}{10}$  took 29.48 c.c. barium hydrate solution; this gave on evaporation and ignition 0.3589 grs.  $\text{BaSO}_4$ , and the same after ignition with sulphuric acid.

These give the strength for the barium hydrate solution as follows:—

| From Titration.    | From $\text{BaSO}_4$ . |
|--------------------|------------------------|
| (i.) 0.10330 N.    | 0.10415 N.             |
| (ii.) 0.10346 N.   | 0.10440 N.             |
| or mean 0.10338 N. | 0.10428 N.             |

Titrated with pure oxalic acid, the strength of the solution was 0.1042 N.

The titration of barium hydrate solution with standard sulphuric acid is then not accurate.

# THE RELATION BETWEEN SPECIFIC GRAVITY, FAT, AND SOLIDS-NOT-FAT IN MILK.

By H. DROOP RICHMOND.

I HAVE collected the results of 328 analyses of milk, and have compared the figures for fat estimated, and that calculated by my "milk scale;" on Table I. are given the results according to percentages of fat.

TABLE I.

| Percentage of Fat. |         | No. of Samples. | Average Error. | Probable Error. | Percentage of results |        |          | Maximum  |         |
|--------------------|---------|-----------------|----------------|-----------------|-----------------------|--------|----------|----------|---------|
| to                 | 1       |                 |                |                 | under 1%.             | to 2%. | over 2%. | + error. | -error. |
| 0                  | to 1    | 40              | +·010          | ±·080           | 60·0                  | 40·0   | 0        | ·19      | ·16     |
| 1                  | to 2    | 11              | +·021          | ±·067           | 63·5                  | 36·5   | 0        | ·13      | ·13     |
| 2                  | to 2·5  | 28              | +·018          | ±·082           | 64·3                  | 28·6   | 7·1      | ·19      | ·22     |
| 2·5                | to 2·8  | 33              | +·007          | ±·064           | 75·8                  | 24·2   | 0        | ·18      | ·17     |
| 2·8                | to 3·0  | 21              | —·012          | ±·068           | 66·7                  | 35·3   | 0        | ·17      | ·16     |
| 3·0                | to 3·25 | 29              | —·027          | ±·069           | 75·9                  | 20·7   | 3·4      | ·12      | ·20     |
| 3·25               | to 3·5  | 39              | —·012          | ±·086           | 74·4                  | 20·5   | 5·1      | ·17      | ·30     |
| 3·5                | to 3·75 | 34              | —              | ±·070           | 76·5                  | 17·6   | 5·9      | ·28      | ·25     |
| 3·75               | to 4·0  | 29              | +·006          | ±·091           | 51·7                  | 44·8   | 3·5      | ·18      | ·28     |
| 4·0                | to 5·0  | 37              | —·046          | ±·107           | 56·8                  | 32·6   | 10·6     | ·15      | ·32     |
| Over 5·0           |         | 15              | +·008          | ±·080           | 60·0                  | 40·0   | 0        | ·15      | ·18     |
| Total              |         | 316             | —·005          | ±·078           | 66·5                  | 29·7   | 3·8      | ·28      | ·32     |

It is seen there that the average difference varies from +·021 with from 1 to 2 per cent. of fat to —·046 with from 4 to 5 per cent. of fat; the total average difference is —·005 per cent.

In Table I. I have rejected 12 analyses, in fact all those milks containing solids-not-fat exceeding 9·5 per cent. as I find that the results calculate too high.

In Table II. I give the whole of the analyses arranged according to percentages of solids-not-fat; those below 8·5 I have grouped together, as these are almost all watered samples; of the others it is seen that the fat calculated exceeds the fat found in proportion as the solids-not-fat rise; the relation between the error and the solids-not-fat is expressed by the formula:  $\text{Error} = \cdot 2 (\text{SNF} - 8\cdot87)$ ; there is no error when the solids-not-fat are 8·87 per cent., which is almost exactly the mean of Vieth's analyses (THE ANALYST, xvii., 84).

TABLE II.

| Percentage of Solids not Fat. |         |     | Number of Samples. |     | Average error. |     | Calculated error. |
|-------------------------------|---------|-----|--------------------|-----|----------------|-----|-------------------|
| Below                         |         | ... |                    |     |                |     |                   |
| Below                         | 8·5     | ... | 110                | ... | —·032          | ... | —                 |
| 8·5                           | to 8·75 | ... | 67                 | ... | —·053          | ... | —·049             |
| 8·75                          | to 9·0  | ... | 79                 | ..  | +·002          | ... | ·0                |
| 9·0                           | to 9·25 | ... | 46                 | ... | +·044          | ... | +·051             |
| 9·25                          | to 9·5  | ... | 14                 | ... | +·091          | ... | +·101             |
| Above                         | 9·5     | ... | 12                 | ... | +·191          | ... | +·186             |

The formula proposed by me (*THE ANALYST*, xiv., 121), does not give such a good agreement as that of Hehner and myself, on which the milk scale is based, though theoretically more correct; the results by the new formula are  $\cdot 03$  lower, and I can find no other formula which does agree so well as the milk scale.

I do not understand why this is so, as the formula of Hehner and myself assumes that volume-percentages and weight-percentages bear a constant relation, whatever the density may be; of course with the small variations in density found in milk, this error is very small, but it is not entirely negligible, as in extreme cases a difference of  $\cdot 05$  per cent. may be observed.

Table II. to some extent explains the differences of average error with varying percentages of fat; unfortunately the presence of many watered milks renders comparison difficult; two of the columns in Table I. (1 per cent. to 2 per cent. and 4 per cent. to 5 per cent.) each only contain two watered milks and these watered milks differ but very slightly in the fat found and calculated. Neglecting these, the average solids-not-fat are 8.95 per cent. and 8.70 per cent. respectively, giving by the formula above, errors of  $+\cdot 016$  per cent. and  $-\cdot 034$  per cent. respectively; curiously these two columns contain the maximum errors, and these agree very nearly with the errors calculated from the solids-not-fat.

I think then the formula may be corrected to read thus:—

$$T - \cdot 254 G = 1.164 F' \text{ and } F = F' - \cdot 2 (\text{SNF} - 8.87);$$

$$\text{or } T - \cdot 254 G = 1.164 (F + \cdot 2 [\text{SNF} - 8.87])$$

this correction is of no practical importance, and may be entirely neglected in ordinary work, as it is almost always within the limit of experimental error.

The reason for the variation of the error with the solids-not-fat is not quite clear.

It may be due to three causes:—

(i.) A change in density due to variation in average composition of the solids-not-fat.

(ii.) Incomplete extraction of the fat.

(iii.) An unrecognised phenomenon.

(i.) It is well known that when a cow gives a milk containing a large amount of solids-not-fat, these solids-not-fat do not have an average composition, but include an excess of albuminoids; in consequence of this the density is lowered, but to explain the variation noticed, a much higher density would be required. I have calculated the necessary composition of the solids-not-fat, to give the required density to explain this for 8.5 per cent., 8.87 per cent., and 9.5 per cent., and find them:

|           |     | Sugar. | Albuminoids. | Ash. |
|-----------|-----|--------|--------------|------|
| 8.5 p.c.  | ... | 4.22   | 4.03         | .75  |
| 8.87 p.c. | ... | 4.80   | 3.33         | .74  |
| 9.5 p.c.  | ... | 6.49   | 2.34         | .67  |



These figures quite preclude the possibility of adopting explanation (i.), unless we assume that the ash increases in greater ratio than the other constituents. No reliable data are at hand to prove or disprove this.

(ii.) While being without actual proof, I think the fact that methods differing so widely in principle as those of Adams, Storch, and Schmid—which are all theoretically near perfection—give identical results, militates strongly against the idea that the fat is underestimated by at least 25 per cent.

(iii.) We must then fall back upon explanation (iii.) that there is an unrecognised phenomenon.

I must frankly confess myself baffled in my search for an explanation, and I have brought this paper before the Society for the purpose of drawing the attention of others to this, in the hope that an adequate explanation may be found; it is possible that the finding of this explanation may considerably aid milk analysis.

This revised formula, when applied to Gamoose milks, gives fairly good results; with goat's milk the calculated fat is about 0.2—0.3 too high.

**The Reichert Process and its modifications.** (*Collected by H. D. Richmond, from the original papers*). Hehner and Angell (*Butter and its Adulterations, London, 1874*) after showing that butter contained more butyric acid than was (then) generally supposed, attempted to estimate this by distillation, but finally relinquished the method on account of discordant results, due largely to the bumping of the liquid and the use of too strong an acid.

Perkins (*THE ANALYST*, iv., 142) published a method for distilling the volatile acid; he used oxalic acid to decompose the saponified butter, and distilled to dryness. Probably he did not obtain the whole of the acid.

In the same year, Reichert (*Zeits.f. Anal. Chem.*, xviii., 68) proposed to saponify 2.5 grammes of butter with caustic soda and alcohol, evaporate off the alcohol, add 50 c.c. of water and 20 c.c. dilute sulphuric acid, and to distil 50 c.c. in a weak current of air. This method, though Reichert himself calls it Hehner's method, is now known as the Reichert process. He showed that butters took a constant amount of deci-normal alkali for neutralization, while fats and artificial butters took very small quantities—0.3 c.c., and cocoanut oil took about 3.5 c.c.; he proposed 14.0 c.c. as the mean for genuine butters and 13.0 c.c. as a limit; he showed also that mixtures of butter and margarine took quantities of 10 alkali equivalent to the amount of butter they contained.

Moore (*Chem. News*, L. 268) in 1884, and Caldwell (*Chem. News*, Liii., 19) in 1886 both speak favourably of the method, the former drawing especial attention to the fact that cocoanut oil, which is not detected by other methods, is shown by the Reichert method.

Medicus and Sheerer (*Zeits. f. Anal. Chem.*, xix., 159) used this method to show that butter on being melted and allowed to cool, separates into portions containing more or less volatile acids respectively.

Allen (*THE ANALYST*, xii., 13) showed that the distilling vessel did not exercise any influence on the results, but that there was a considerable loss on saponification in an open basin, and recommended a closed flask; this loss was due to the formation of butyric ether, as had been already pointed out by Hehner and Angell (*loc. cit.*). Wanklyn and Fox actually estimated the butyric ether formed by saponifying with a barely sufficient quantity of soda (*THE ANALYST*, ix., 73), but naturally always fell far below the total quantity.

Munier (*Zeits. f. Anal. Chem.*, xxi., 394) proposed the use of an alcoholic potash solution for saponification and phosphoric acid to liberate the acids.

The results found by various observers are given in the following table:—

| Name.   | No. of Samples. | Limits.       |
|---|-----------------|---------------|
| Reichert ( <i>loc. cit.</i> )... ..                         | 13              | 13.0 — 14.95  |
| Caldwell ... ..   | ?               | 12.7 — 15.5   |
| Schmitt ... ..  | ?               | 13.0 — 14.3   |
| Allen ( <i>THE ANALYST</i> , x., 103) ... ..                | ?               | 12.5 — 15.1   |
| Ambuhl ( <i>Zeits. f. Anal. Chem.</i> , xix., 159) ...      | ?               | 14.05 — 15.55 |
| Munier ( <i>loc. cit.</i> ) ... ..                          | 66              | 9.2 — 14.05   |
| Reichardt ( <i>Zeits. f. Anal. Chem.</i> , xxiii., 565) ... | 35              | 13.8 — 14.7   |
| Beckhurts ( <i>Jahr. d. Chem. Tech.</i> , 1883, 978) ...    | ?               | 15.6 — 17.5   |
| Merckling ( <i>Pharm. Zeit.</i> , 1882, 643) ... ..         | ?               | 13.2 — 13.55  |
| Woll ( <i>Zeits. f. Anal. Chem.</i> , xxvi., 28) ... ..     | 10              | 12.0 — 14.9   |
| Cornwall and Wallace ( <i>Ditto</i> xxvi., 28)... ..        | 80              | 11.3 — 15.1   |
| Nilson ( <i>Centralb. f. Agrikulturchemie</i> , 1887, 171)  | ?               | 9.27 — 20.5   |

Too much importance must not be attached to these figures, as they were obtained by the original form of the method (or very slight modifications); Munier's low results have been criticised by Wollny (*post*), and Nilson's have also been doubted, though on no very strong grounds.

Nilson showed that disease may seriously reduce the volatile acids; one cow whose butter gave 16.85 c.c., after a few day's illness yielded butter taking only 10.1 c.c. of  $\frac{N}{100}$  alkali. His lowest result, 9.27 c.c., was obtained from butter prepared from the milk of a cow directly after parturition, and he shows that the quantity of volatile acids rapidly increases, and becomes normal a very short time after calving. Figures as low as 9.27 can then hardly be considered normal for commercial butter.

Meissl (*Dingl. Pol. Journ.*, 233, 229) proposed to saponify 5 grammes of butter-fat in a flask of about 200 c.c. capacity with 2 grammes of caustic potash and 50 c.c. of 70 per cent. alcohol, and to drive off the alcohol on the water bath. The resulting soap

is dissolved in 100 c.c. of water, and 40 c.c. of dilute sulphuric acid (1 to 10) are added and the solution distilled with a few small pieces of pumice; 110 c.c. are collected, filtered, and 100 c.c. titrated with deci-normal alkali. In common with Reichert and the earlier experimenters, he used litmus as an indicator, but the superiority of phenol-phthalein for this purpose soon became apparent to many. To the number of cubic centimetres of  $\frac{N}{10}$  alkali one tenth is added; he found thus that butters gave from 26.6 c.c. to 31.8 c.c., and fats and artificial butters about 3.0 c.c.

Sendtner (*Rep. d. Anal. Chem.*, i., 137) as early as 1883 proposed 23 c.c. as the lowest limit.

Hansenn (*Studien u. d. Chem. Nachweis Fremder Fetten. Butter. Erlangen*, 1884, 26), proposed blowing into the flask in order to drive away the last traces of alcohol, and was one of the earliest to use phenol-phthalein as indicator.

This method was adopted by the Congress of Bavarian Analytical Chemists, at Monaco, in 1883; Meissl's limit of 26 c.c. was, however, considered not to be universally applicable, and 23 c.c. was taken. The Paris Municipal Laboratory also adopt it with the modification of saponifying in an open basin, transferring the soap to a flask, and washing the basin with 100 c.c. of hot water; their limits are stringent: 26 c.c. to 33.5 c.c.

The following figures are published:—

|  |     |     |     |            |             |
|--|-----|-----|-----|------------|-------------|
| Meissl ( <i>loc. cit.</i> )              | ... | ... | ... | 52 samples | 26.6 — 31.8 |
| Sendtner ( <i>loc. cit.</i> )            | ... | ... | ... | 55 „       | 24.0 — 32.8 |
| Hager ( <i>Chem. Centr.</i> , 1886, 495) | ... | ... | ... | ?          | 26.0 — 31.0 |

Wollny, in a now classic memoir (*Milch Zeitung*, 1887: 32, 609; 33, 630; 34, 651; and 35, 669; translated in *THE ANALYST*, xii., 201, *et seq.*), studied the errors of the Reichert-Meissl process; these are:—

- (1). Error due to the absorption of carbonic acid during the saponification (may amount to + 10 per cent.)
- (2). Error due to the formation of ethers during saponification (may amount to — 8 per cent.)
- (3). Error due to the formation of ethers during the distillation (may amount to — 5 per cent.)
- (4). Error due to the cohesion of the fatty acids during distillation (may in extreme cases amount to — 30 per cent.)
- (5). Error due to the shape and size of the distilling vessel and to the time of distillation (may vary the results  $\pm$  5 per cent.)

To avoid these errors he lays down the following method of working:—

Five grammes of butter-fat are weighed into a round flask of about 300 c.c. capacity, with a neck 2 c.m. wide and 7 to 8 c.m. long; 2 c.c. of a 50 per cent. soda solution and

10 c.c. of 96 per cent. alcohol are added, and the flask heated for half-an-hour on the water bath under a slanting inverted condenser; between the condenser and the flask is a T piece, which is closed, the limb being turned upwards. At the expiration of half-an-hour the limb of the T piece is opened and turned downwards, and the alcohol distilled off during a quarter-of-an-hour; 100 c.c. of boiling water are added by the T piece, and the flask heated on the water bath till the soap is dissolved. The solution is allowed to cool to 50° or 60°, 40 c.c. of dilute sulphuric acid (25 c.c. to a litre; 2 c.c. of soda solution should neutralize about 35 c.c. of this) and 2 pieces of pumice the size of peas are added. The flask is at once furnished with a cork carrying a tube 0.7 c.m. in diameter having 2 c.m. above the cork, a bulb 2 to 2.5 c.m. in diameter; above this the tube is bent at an angle of 120° and 5 c.m. further on again at an angle of 120°; this tube is joined to a condenser by an indiarubber tube. The flask is heated by a very small flame till the fatty acids are all melted, and the flame is then turned up and 110 c.c. distilled off in from 28 to 32 minutes. The distillate is well mixed, and 100 c.c. are filtered off through a dry filter, 1 c.c. of a 0.05 per cent. solution of phenol-phthalein solution in 50 per cent. alcohol added, and the solution titrated with  $\frac{N}{10}$  baryta solution. To the figure thus obtained one-tenth is added, and the amount found by a blank experiment subtracted; the blank should not exceed 0.33 c.c.

In order to render this method more sensitive, if possible, for the detection of small quantities of butter in margarine, Hehner proposed the use of 5 c.c. only of alcohol, saponifying (almost instantaneously) in a closed flask, warming for five minutes with occasional shaking, and driving off the alcohol through a narrow tube in a cork, reduced pressure being applied towards the end, and the addition of 100 c.c. of water which has boiled at least half an hour. He finds the blank figure thus to be less than 0.1 c.c., and the same as that given by 100 c.c. of boiled water filtered through a dry filter; other fats and oils give less than 0.06 c.c., and no increase is observed in heating them on the water bath with the soda solution for two hours.

In order to facilitate the melting of the fatty acids, Richmond (*THE ANALYST*, xiv., 112) proposes lengthening the bulb tube, used by Wollny for distillation, above the bulb to 15 c.m. and placing on it a small condenser, through which water is kept running during the melting of the acids, this being removed during distillation; the same results are obtained by the use of this apparatus as by Wollny's.

Mansfeld (*Milch. Zeitung*, 1888, 15, 281) saponifies in a closed flask for two hours on the water bath with a solution of 56 grammes of potash in 100 grammes of water, no alcohol being used; he operates otherwise as Wollny. His method gives the same results as that due to Wollny. His blank is .4 c.c. and the extremes are 24.42 to 33.15 for butters and 0.59 to 0.96 for margarines.

Goldman (*Chemiker Zeitung*, 1888, 12, 183; 14, 216, and 20, 317) distills the whole of the volatile acids in a current of steam, collects 600 c.c. of distillate, and titrates

with  $\frac{8}{10}$  baryta. He finds as limits 36.24 c.c. to 43.20 for butter, and 0.80 to 0.92 for margarine; duplicates do not differ by more than 0.2 c.c. Two samples gave by this method 36.24 and 36.28 c.c., and by the Reichert-Wollny-Mansfeld process 27.00 and 28.04 c.c. respectively.

Leffmann and Beam (*THE ANALYST*, xvi., 153) saponify with 2 c.c. of caustic soda solution in 10 c.c. of glycerine, heating over a naked flame with constant shaking. As in the reaction heat is evolved, care must be exercised; they otherwise operate as Wollny. The results are about 0.2 c.c. higher than Wollny's.

The Reichert-Wollny method is largely adopted in every country except France, and may be considered as a standard method.

In England the proportions of the Reichert method with Wollny's precautions are much used; Richmond (*Stat. Sper. Agraria Ital.*) has determined the ratio between figures obtained thus, and by the Reichert-Wollny method and finds it to be 2.21 to 2.27, mean 2.23. Were the acid all butyric, the ratio would be 2.167. His experiments show that the volatile acids of butter do not distil as if they consisted solely of butyric acid and its homologues, but indicate the presence of another acid: he suggests lactic acid.

The following limits have been found by various observers:—

| Name.  | No.<br>Samples. | Limits.       |
|--|-----------------|---------------|
| Allen ( <i>THE ANALYST</i> , xv. 4) ... ..   | 2               | 22.5 — 24.55* |
| Stein ( <i>quoted by Allen, loc. cit.</i> ) ... ..                                     | ?               | 25.08 — 31.95 |
| Mansfeld ( <i>loc cit.</i> ) ... ..  | 88              | 24.42 — 33.15 |
| Besana ( <i>Stat. Sper. Ag. Ital.</i> , xvi., ) ... ..                                 | 114             | 21.8 — 30.19  |
| Sartori ( " " ) ... ..   | 52              | 23.59 — 30.79 |
| Vigna ( " " ) ... ..   | 23              | 20.68 — 31.79 |
| Spallanzani " " ) ... ..   | 70              | 20.63 — 30.6  |
| Longi ( " " ) ... ..   | 26              | 22.55 — 28.4  |
| Maissen and Rossi " " ) ... ..   | 20              | 21.56 — 26.40 |
| Schrodt ... ..   | —               | —             |
| Mayer ( <i>Landw. Verss.</i> xxxv., 261) ... ..  | 20              | 20.3 — 33.5   |
| Vieth ( <i>THE ANALYST</i> , xiv., 67, 147; xv. 44;<br>xvi., 62, 172; xvii. 62) ... .. | 236             | 20.0 — 32.5   |
| F. Jean ( <i>Rev. Int. d. Falsif.</i> , 1891, 65) ... ..                               | 1               | 20.75         |

Vieth and Spallanzani have also found in samples obtained under exceptional circumstances, which cannot be considered as commercial butter, as low as 14.7 c.c. and 14.3 c.c. respectively.

\* These were very exceptional samples, and hence the figures are not representative of the ordinary composition of butter-fat.

The average of the results of different observers (excluding Vieth, who searched for low samples) shows that out of 100 samples—

|    |                                   |
|----|-----------------------------------|
| 3  | will probably give over 30 c.c.   |
| 85 | „ „ „ between 30 c.c. and 26 c.c. |
| 8  | „ „ „ „ 26 c.c. and 25 c.c.       |
| 3  | „ „ „ under 25 c.c.               |

The absolute lower limit must be fixed at 20 c.c. for butters, but all samples giving below 25 c.c. may be looked upon as suspicious, and with a probability of 3 to 100 against such samples being genuine: 25 c.c. may be adopted as a commercial limit. But it must be remembered that the English law gives all probability to the benefit of an accused person.

H. D. R.

[NOTE BY H. D. R.—Löffmann and Beam's modification has the advantages over the Reichert-Wollny method of yielding a clear distillate and giving a sharper end reaction.]

**Butter-fat.** M. Schrodtt and O. Henzold. (*Landw. Versuchs.*, 1892, xl., 229, through *Chem. Zeit.*)—The authors have examined the butter from a herd of 220 to 230 cows weekly for one year. They have arrived at the following conclusions:—

(1). The content of the butter-fat in volatile fatty acids is dependent upon the period of lactation, and is not influenced by the fodder. Diminution of the quantity of volatile fatty acids occurs as lactation advances.

(2). As a rule, a low proportion of volatile fatty acids, while being independent of the fodder, corresponds with a high proportion of insoluble fatty acids, the co-efficient of refraction being thereby raised.

(3). Some samples of butter-fat have a noticeably low content of volatile fatty acids; no satisfactory reason has yet been assigned for this phenomenon.

(4). In consequence of the low limit that can be fixed for the volatile fatty acids, the determination of these constituents for the purpose of checking sophistication, is not completely conclusive. It is, therefore, advisable to estimate also the insoluble fatty acids, and the co-efficient of refraction.

B. B.

**Determination of Aluminium in Steel and Alloys.** W. Schoenels. (*Stahl und Eisen*, 1892, xi., through *Chem. Zeit.*)—Five to ten grams of drillings of the metal are dissolved in nitric acid of sp. gr. 1.2, in a platinum dish, evaporated to dryness, and ignited cautiously until all nitrous fumes have ceased. The oxides thus left are ground in an agate mortar, fused with caustic potash free from alumina in a silver dish, then well extracted with water, the filtrate acidulated with hydrochloric acid and precipitated

with ammonia, the alumina being then collected, ignited and weighed. The alumina thus obtained from basic steel is free from silica, but that from Siemens-Martin steel, crucible steel and ferro-aluminium, is contaminated with that substance, and it is, therefore, removed by subsequent treatment with hydrofluoric acid. The beakers used in the analysis must be boiled out with acid. The results bear out the claim of the process to be considered accurate, and a steel containing 0.01 per cent. of Al can be distinguished with certainty from one free from the metal. The method can be used for copper, bronze, and the like.

B. B.

**New Method for Estimating Vanadic Acid.** A. Rosenheim and C. Friedheim. (*Zeit. für Anorg. Chem.*, 1. 313-317.)—In the presence of allied acids, such as phosphoric, tungstic and molybdic acids, it is very difficult to separate vanadic acid in a weighable form. Hitherto reduction with sulphurous acid and subsequent titration with permanganate, or distillation with hydrochloric acid in presence of potassium bromide and absorption of the evolved halogen in potassium iodide, followed by titration of the liberated iodine, have been the methods generally employed for estimating this acid. But of these two methods the former is inapplicable in presence of molybdic and arsenic acids, and the latter is objectionable as introducing potassium, and thus preventing a determination of the alkalis in the same portion.

The author finds that the reaction, first observed by Berzelius, between vanadic anhydride and oxalic acid takes place exactly according to the equation  $V_2O_5 + 11_2 C_2O_4 = V_2O_4 + H_2O + 2 CO_2$ ; and thus serves as a basis for the quantitative determination of the vanadic acid, even in presence of the above mentioned other acids, neither of them being reduced by oxalic acid.

The vanadate, or mineral containing vanadate, is dissolved with the aid of sulphuric acid, the solution mixed with about an equal volume of saturated oxalic acid solution, and heated with more sulphuric acid, if necessary, in a flask connected with an apparatus for absorbing and weighing the evolved carbon dioxide. Every 48.246 parts of carbon dioxide evolved represent 100 parts of vanadic anhydride.

A. G. B.

**Estimation of Potassium as Perchlorate.** W. Wense. (*Zeits. f. Angew. Chem.* 1892, 233-234.)—The author uses the perchlorate method to his entire satisfaction. (THE ANALYST, 1892, 57.) The perchlorate should be obtained in as granular a form as possible; to this end much free acid is first eliminated by evaporation to dryness, the residue dissolved, the solution warmed on the water bath, and  $1\frac{1}{2}$  to  $1\frac{3}{4}$  times as much perchloric acid as is equivalent to the amount of potassium supposed to be present dropped in. Ten to twelve properly granular precipitates can be filtered and washed in an hour,

and four hours will suffice for 13 to 14 determinations. To avoid the precipitation of sulphuric acid when present, evaporate with sufficient perchlorate to decompose all chloride, wash with alcohol as usual, dissolve in hot water, evaporate to dryness and ignite strongly enough to convert the potassium perchlorate into potassium chloride, dissolve in water and estimate the chloride by standard silver solution. The method is cheaper than the platinum process. For 5,000 potash determinations some 20 kilos of potassium chlorate and the same quantity of sulphuric acid would be sufficient without recovering the perchloric acid from the precipitates.

A. G. B.

**The Estimation of Nicotine in Tobacco-extract.** J. Pinette. (*Chem. Zeit.*, xvi., 1072.)—Tobacco-extract is now an article of commerce of considerable importance. It is chiefly used as an insecticide for cattle, and has hitherto been valued by its specific gravity, but a more exact method is now necessary. The determination of the nicotine has been somewhat discredited as a means of valuation, on account of the want of concordance of the results of different analysts. In order to make some advance towards a standard method that may be generally accepted, the author proposes the following process:—

Ten grams of the extract are made up to 50 c.c. and 10 c.c., placed in a graduated separator of 200 c.c. capacity. About 30 c.c. of dilute caustic soda solution are added, and then ether until the total bulk is about 150 c.c. The separator is shaken until the nicotine is all dissolved out by the ether, the volume of the ethereal solution read off, 25 c.c. pipetted into a dish, allowed to evaporate spontaneously, and titrated with decinormal sulphuric acid, using cochineal as an indicator. 1 c.c. of the acid equals 0.0162 grms. of nicotine. The samples examined used 0.2 to 1.8 c.c. of acid, the content of nicotine therefore ranged from 1 to 9 per cent.

The following method, which is, however, considerably more laborious, was used to check the results. 10 grms. of the sample are diluted, made alkaline and distilled in a current of steam, until the distillate measures about 500 c.c. It is then made slightly acid with sulphuric acid, evaporated to about 25 c.c., and titrated with potassium mercuric iodide solution. The latter is prepared according to Kissling's prescription, thus: 87.5 grms. of potassium iodide are dissolved in 250 c.c. of water, and 40 grms. of mercuric chloride in 750 c.c. of (hot) water. The mercuric chloride solution is then poured into the potassium iodide until a permanent precipitate is produced, which is allowed to subside, and removed by filtration through asbestos. The resulting solution measures about 1 litre, and will keep well in the dark. 0.1 gram of nicotine requires 15 to 20 c.c. for precipitation. The exact value is determined by standardizing the solution on pure nicotine under similar conditions. The titration is performed until the addition of the potassium mercuric iodide solution gives no further turbidity. When nearing the end of



the titration, it is best to pour off the clear fluid and add a little more of the reagent, pouring it back again if a precipitate is produced, and shaking it up with the previous precipitate, which induces speedy separation.

B. B.

## REVIEW.

*Watts' Dictionary of Chemistry*:—Revised and entirely re-written by H. Forster Morley, M.A., D.Sc., and M. M. Pattison Muir, M.A. Vol. III. Longmans, Green & Co.

*Watts' Dictionary of Chemistry* is such a well-known and deservedly appreciated compilation that the appearance of the third volume of the edition now being produced by Professors Morley and Pattison Muir will be welcomed by chemists of every denomination.

The volume under notice contains a number of admirable articles by special contributors, among which that on "Isomerism," by Dr. H. E. Armstrong, and "Metals, Rare," by Mr. William Crookes, deserve honorable mention.

It is to be regretted that all the special articles are not of equal value. Among them stands out prominently, for its imperfections and inaccuracies, that on "Milk," contributed by Dr. W. G. Halliburton, B.Sc., F.R.S. It is unfortunate that an article of such a character should have found a place in the pages of *Watts' Dictionary*.

Referring to the composition of butter, on page 406, Dr. Halliburton states that:—"The fats present are olein, much palmitin, much less stearin; and about 2 per cent. of the total fats consist of the triglycerides of butyric, caproic and caprylic acids, with traces of myristic and arachidic acids. Cow's butter contains about 68 per cent. palmitin and stearin, 30 per cent. olein, and 2 per cent. of the other fats mentioned." Dr. Halliburton is clearly unaware that in the ordinary process of analysis chemists are in the habit of separating over 5 per cent. of volatile acids from butter-fat.

On the succeeding page is a column headed "Analysis of Milk," and in this occur the following methods for determining the solids and butter. "*Solids*.—To 10 grains (*sic*) of dry sand add 5 c.c. of milk, and dry at 100° to constant weight. The increase in weight gives the solids in 5 c.c. of milk. Below 10.5 p.c. of solids in cow's milk indicates dilution. *Butter*.—This may be estimated by weighing the amount of residue from an ethereal extract of milk to which an equal volume of 10 p.c. caustic potash has been added. The normal minimum for fat is about 2.75 p.c. (Cameron)." This is the sum of the information given on the subject of estimation of total solids and fat in milk, and certainly cannot be said to do the subject justice. By public analysts, and other readers of *THE ANALYST*, such statements would be simply the subject of ridicule, were it not that their occurrence in a standard compilation like *Watts' Dictionary* is likely to be fraught with permanent mischief.

The Editors have, in the present edition, systematically relegated analytical processes to another place, simply recommending the readers to "consult Manuals of Analysis." The wisdom of this policy is fairly open to question, and many besides professional analytical chemists have had cause to lament the absence from the new edition of *Watts' Dictionary* of the full information on analytical matters which was a valuable feature of the first edition. But where analytical processes are described at all, care should be taken that they are described accurately. Possibly editorial revision of Dr. Halliburton's article was considered unnecessary; but in the case of articles contributed by the Editors themselves, the same excuse does not apply. Thus the methods of estimating manganese, as given on page 179, afford a remarkable instance of the slovenly manner in which analytical facts are treated. There the readers are told that "Mn is usually estimated gravimetrically by pptn with  $\text{NH}_3\text{aq}$ , heating the ppt in air and weighing as  $\text{Mn}_2\text{O}_3$ ." Even tyros in analysis will open their eyes at being directed to precipitate manganese with ammonia!

On page 124, in reference to the detection of lead, it is stated that "the  $\text{H}_2\text{S}$  test is said to detect 1 pt. of lead in 100,000 pts. of water; the  $\text{H}_2\text{SO}_4$  test 1 pt. in 20,000; and the  $\text{K}_2\text{CrO}_4$  test 1 pt. in 70,000."

Surely it should be well known that one-tenth of the quantity of lead said to be recognisable by sulphuretted hydrogen and chromate of potassium can be readily detected by the simple addition of the reagent to the liquid, without using any special device to increase the delicacy of the tests. Again, it should be obvious to the editors of *Watts' Dictionary* that a test which detected only one grain or two-thirds of a grain of lead per gallon of water would be practically valueless.

Unfortunately the same weakness of description is to be found in other directions besides that of analytical methods. Thus, under the head of phenol, the behaviour of the substance with neutral solvents is limited to statements of its behaviour with water, alcohol and ether; and even then the solubility in water is seriously misstated. But in the last respect the editors only err in company with most other authorities, including Beilstein. The reader is left wholly without information as to the behaviour of phenol with such solvents as chloroform, benzene, petroleum ether, or oils; nor do the editors appear to think the well-known crystalline compound of phenol with water, of the formula  $2\text{C}_6\text{H}_5\text{O} + \text{H}_2\text{O}$ , discovered and habitually manufactured by Mr. Charles Lowe, worthy of mention.

Of course *Watts' Dictionary* is indispensable to the advanced student of chemistry; but it is to be regretted that, having gleaned all he can from its pages on a particular subject, he will have to verify and supplement the information by reference to other works of a far less pretentious kind. That such should be the case is to be lamented on every ground, especially since new editions of *Watts' Dictionary* are not produced every day.

# THE ANALYST.

OCTOBER, 1892.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

### ON THE DETERMINATION OF OLEIC ACID.

By OTTO HEHNER.

*(Read at Meeting, June 30th, 1892.)*

BEING lately desirous of estimating the amount of olein in butter-fat, and of determining whether the whole of the iodine absorption of butter-fat could be calculated into olein, or whether there was any foundation for the statement made by Koefoed that other still more unsaturated fatty acids were present, I attempted the separation of the lead-salts by means of ether in the usual manner. The method in question was first proposed by Varrentrapp, and afterwards variously modified by Oudemans, Kremel, and Muter; but as these chemists had not the advantage of being able to test the various products by Huebl's Iodine Absorption Method, which sharply distinguishes saturated from unsaturated fatty acids; and as I had previously found that the lead salts of the higher saturated fatty acids were not by any means insoluble in ether, I thought it desirable to submit the method to a critical examination.

Ten grammes of butter-fat were saponified with alcoholic potash, the alcohol driven off, the soap rendered perfectly neutral, and the aqueous solution precipitated with neutral lead acetate. The precipitate was collected, pressed, and air-dried. It was then extracted in a Soxhlet tube with ether. After many hours' extraction, the soluble portion was decomposed with hydrochloric acid in the presence of ether, the ether solution of the fatty acids well washed with water, the ether evaporated in a current of carbonic acid, and the fatty acids dried in that gas till constant in weight. 32.1 per cent. of fatty acids were thus obtained, which showed an iodine absorption of 58.04 per cent.

The extraction of the insoluble lead salts with ether was then continued for some hours, and 3.95 per cent. of dissolved fatty acids were obtained with an iodine absorption of 55.48 per cent. By persistent extraction a third fraction was obtained, amounting to 3.68 per cent., with an iodine figure of 59.18 per cent. The lead-salts which had remained undissolved in ether were then decomposed with hydrochloric acid, and dried in carbonic acid to constant weight. 42.53 per cent. were obtained, with an iodine

absorption of 18.60 per cent. Thus altogether 82.27 per cent. of fatty acids were obtained, a figure which falls short somewhat of the actual quantity present in the sample of butter-fat, but it is almost impossible so to manipulate the sticky lead-precipitates as to avoid some loss.

It is obvious from this experiment, that although the extraction with ether lasted for several days, a complete separation of the salts of the saturated fatty acids from those of the unsaturated ones had not been obtained. The iodine absorption of even the first soluble portion was far too low for pure oleic acid, which is 90.1 per cent., and the saturated fatty acids had evidently dissolved in abundance. It is equally clear that, in spite of the protracted treatment with ether, the remaining lead-salts still included a considerable proportion of unsaturated fatty acids.

The equivalent of the first portion of ether-soluble acids was found to be 256.8, and that of the remaining insoluble acids 254.7.

As these results might have been attributed to the complicated composition of butter-fat, and to the presence on the one hand of unsaturated fatty acids with insoluble lead-salts, or to the solubility of the lead-salts of the lower fatty acids, I made a similar attempt to estimate the olein in a sample of margarine, which had been prepared from animal fats only, and which did not contain more than a mere trace of butter-fat obtained from the milk employed in its manufacture.

The lead-salts were extracted for two days with ether, the residue dried, ground up finely, and once more extracted for some time. The soluble lead-salts thus obtained amounted to 48.1 per cent., and had an iodine absorption of 64.88 per cent., while the insoluble lead-salts furnished 46.0 per cent. of fatty acids, with an iodine absorption of 17.72.

Here no low fatty acids were present that could complicate the result, nor, in all probability, any unsaturated fatty acids with less hydrogen than oleic acid; and yet nothing like pure oleine had been obtained, nor had the whole of the unsaturated fatty acid been removed by the persistent extraction with ether.

The lead-salts from cotton-seed oil dissolved almost completely in ether, and yielded an ether-soluble acid portion with 116.26 iodine absorption. The small portion which was insoluble in ether gave fatty acids with an iodine figure of 35.3. The cotton oil employed absorbed 108.6 per cent. of iodine.

A sample of almond-oil, with an iodine figure of 98.87, also yielded a lead-soap which was almost completely dissolved by ether in a few hours, the soluble portion of the fatty acids absorbing 100.67 and the small insoluble portion 98.71 per cent. of iodine.

From a sample of cocoa-nut oil, which showed an iodine absorption of 8.22 per cent., 63.49 per cent. of acids whose salts were soluble in ether were obtained, and 19.58 per cent. of insoluble acids. The former absorbed 10.49 per cent. of iodine, the latter 0.69. This latter small figure is within the limits of experiment, and it appears as if the olein

of cocoa-nut oil could be completely washed out by abundance of ether from the lead-salt, but nothing like an estimation was evidently possible, as a far larger amount of saturated fatty acids passed into the ether solution than of lead oleate.

These figures show most conclusively to my mind that the method of olein determination, which is founded upon the relative solubilities of the lead-salts in ether is utterly untrustworthy. Neither are the lead-salts of the saturated fatty acids sufficiently insoluble, nor the unsaturated lead-salts so easily soluble as to allow of a separation useful for analytical work. Sometimes the two sources of error may counter-balance each other. Thus in the sample of butter-fat, to which I referred in the beginning of this note, the iodine absorption was 33.32 per cent., corresponding to 38.6 per cent. of olein (assuming that the whole of the iodine absorption was due to olein only), and the soluble portion obtained by lengthy extraction amounted to 39.7 per cent., but this is obviously only a coincidence, as in no case was the iodine absorption of the soluble fractions more than 59 per cent., which figure is only about two-thirds of the iodine absorption of oleic acid. By less protracted extraction, such as the mere shaking out of the lead-precipitate with ether for a short time, a purer olein may possibly be obtained, but a still larger portion of olein than that shown in the above experiments would be left undissolved with the saturated lead-salts.

Since carrying out my experiments my attention has been drawn to an investigation of the Sawarri nut by Lewkowitsch (*Soc. Chem. Ind.* 1890, 845), in which a separation of the lead-salts was also attempted by means of ether, with unsatisfactory results.

I beg to record my obligation to my assistant, Mr. W. P. Skertchley, for carefully carrying out most of the analytical work recorded in this paper.

#### DISCUSSION.

Mr. A. H. Allen said he had listened, and he was sure that all present had listened, with very great interest to the very important, novel, and suggestive communication which had been made by the President. The subject furnished another illustration of the proverb, "put not your trust in book-makers." It was a most unfortunate thing that a large number of statements which appeared in standard works had no foundation in fact, and got repeated from one book to another to the great detriment of workers. Mr. Hehner had shown the unreliability of the usual process employed for separating oleic acid from acids of the stearic series. They were literally deprived of the only method which had been thought capable of giving anything like a reasonably accurate estimation of the actual proportion of oleic acid in a mixture, and that being the case it remained to be seen what else could be done in this direction. It was possible that a change of solvent might answer. The change from ether to petroleum spirit might effect a sharper separation of the lead oleate from the lead-salts of the saturated acids, and some modification of that sort might be found feasible.

## THE DETERMINATION OF CARBON DIOXIDE IN THE AIR OF BUILDINGS.

BY AUGUSTUS H. GILL, PH.D.

IN the only treatise upon air analysis in the English language, the method given for the determination of carbon dioxide admits of no great accuracy, as results varying 6 per cent. from an average, and 10 per cent. among themselves, would indicate. The writer recommends the following method, which has been in use in his laboratory in almost the present form for fifteen years.

Both methods are those of Pettenkofer,\* which consists in bringing a large known volume of air in contact with standard barium hydrate solution.

The bottles used for containing the samples are ordinary green glass gallon or two gallon bottles, holding 4,400 or 8,800 c.c. respectively; they are calibrated with water, by weighing upon scales sensitive to 5 gms., and their capacity marked upon them with a diamond. They may be conveniently transported from place to place in a partitioned basket made for the purpose.

The bellows there suggested (wooden discs joined by a strip of rubber, with no valves) was found troublesome to manipulate, and has given way to one about to be described. The nozzle of an ordinary 9-inch blacksmith's bellows is removed and the opening fitted with a valve opening outward; this is made by tying a bit of chamois skin over a cork which fits over a tube passing into the nozzle opening. By varying the position of the cork, different degrees of tightness of valve are attained. To the other opening of the bellows, closed with its usual valve, is fitted a cork carrying a four-foot piece of  $\frac{5}{8}$ -inch rubber tubing terminating in a light two-foot brass tube, bent for insertion into the bottles. Instead of the bellows, a small 6-inch fan blower, the driving parts of which are connected by rubber bands to render it noiseless, can be used if it is desired to decrease the bulk of the apparatus.

The bottle is fitted with a rubber stopper, carrying a glass tube, closed by a small unperforated rubber nipple; both the stopper and nipple have been digested with caustic potash and thoroughly washed to remove the superficial zinc oxide.

The air to be tested is drawn into the bottle by means of the bellows, fifteen strokes being taken, sufficing to fill a four litre bottle four times, thus insuring a representative sample. In collecting this sample the atmosphere in the room should be as quiet as possible; care must be exercised to avoid the drafts or the proximity of people.

When used the bottles should be *clean* and *dry*; by *clean* is understood containing nothing to affect the barium hydrate used. When wet the standard barium hydrate is diluted, and as the whole of it is not used, the determination is lost, unless the amount of water present be accurately known.

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\* *Annalen*, 2, Supp. Band, p. 1.

The operation of drying the bottles is by no means as troublesome as it would appear. A small closet heated by steam and provided with suction, enabling a current of hot air to be drawn into the bottles, suffices to dry a dozen bottles in half an hour. The samples are brought into the laboratory, the temperature of which should be a little higher than that of the place where they were taken, and allowed to stand half an hour, or until they have attained its temperature.

50 c.c. of the standard barium hydrate are now run in rapidly from a burette (the tip passing entirely through the tube in the stopper), the nipple replaced, and the solution spread completely over the sides of the bottle while waiting three minutes for the draining of the burette, before reading, unless it be graduated to deliver 50 c.c. The bottle is now placed upon its side, and shaken at intervals for 40–60 minutes, taking care that the whole surface of the bottle is moistened with the solution each time. The time of absorption, ten minutes, recommended in the treatise, is much too short, as the disappearance of the last traces of carbon dioxide is very slow indeed, half an hour in many cases being insufficient.

At the time at which the barium hydrate is added, the temperature and pressure should be noted. At the end of the above period, shake well to insure homogeneity of the solution, remove the cap from the tube, and invert the large bottle quickly over a 50 c.c. glass stoppered bottle, so that the solution shall come in contact with the air as little as possible. Without waiting for the bottle to drain, withdraw a portion of 15 or 25 c.c. with a narrow stemmed spherical bulbod pipette and titrate with sulphuric acid\* (1 c.c. equals 1 mgm.  $\text{CO}_2$ ) using rosolic acid as an indicator. The difference between the number of cubic centimetres of standard acid required to neutralize the amount of barium hydrate (e.g., 50 c.c.) before and after absorption, gives the number of milligrams of carbon dioxide present in the bottle.

This is expressed in cubic centimetres under standard conditions, and divided by the capacity of the bottle under standard conditions, and the results reported in parts per 10,000. To reduce the air in the bottle to standard conditions, a hygrometric measurement of the air in the room from which the sample was taken, is necessary. This in ordinary cases is usually omitted, as the object of the investigation is *comparative* results, as regards the efficiency of ventilation, and the rooms in the same building would not vary appreciably in the amount of moisture in the atmosphere. This correction may make a difference of about 0.15 parts per 10,000.

Some of the results obtained by our students by the preceding method are as follows:—

\* Sulphuric acid, in distinction to oxalic acid, enables one to estimate the excess of barium hydrate in presence of the suspended barium carbonate, and also of caustic alkali, which is a frequent impurity of commercial barium hydrate. Professor Johnson, in the American edition of *Fresenius' Quantitative Analysis*, calls attention to the fact that the normal alkaline oxalates decompose the alkaline earthy carbonates, so that the reaction continues alkaline if the least trace of soda or potash be present. The sulphuric acid may be prepared by diluting 46.51 c.c. normal sulphuric acid to a litre.

*Expressed in parts of CO<sub>2</sub> per 10,000.*

| Room No. 24. | No. 43. | No. 37. | No. 34. | No. 34. | No. 23. | Outside Air. |
|--------------|---------|---------|---------|---------|---------|--------------|
| 5.54         | 7.34    | 4.94    | 5.16    | 5.53    | 4.54    | 3.13         |
| 5.59         | 7.27    | 4.89    | 5.12    | 5.52    | 4.46    | 3.09         |

The subjoined results are interesting as showing rate of vitiation of the air in a well-ventilated lecture room. It is 15 feet high, having a capacity of 24,000 cubic feet, and supplied with 185,000 feet of air per hour, from three flues; 225 students were present.

|                      | Time. | 1st Day.<br>Pts. CO <sub>2</sub> in 10,000. | 2nd Day. |
|----------------------|-------|---|----------|
| Before lecture .. .. | 11.35 | 3.89  | 4.54     |
|                      | 12.10 | 6.07  | 9.93     |
|                      | 12.20 | 8.44  | 10.27    |
|                      | 12.30 | 11.29                                       | 10.43    |
|                      | 12.40 | 11.38                                       | 10.50    |
|                      | 12.50 | 10.56                                       | 10.58    |
| End of lecture .. .. | 1.00  | 6.62  | 7.19     |
|                      | 1.30  | 3.72  | 6.10     |

The following shows the distribution of carbon dioxide in an ordinary theatre:—

|                     | CO <sub>2</sub> per 10,000. |
|---------------------|-----------------------------|
| Floor .. .. .       | 39.13 pts.                  |
| 1st Balcony .. .. . | 42.86 "                     |
| 2nd Balcony .. .. . | 44.72 "                     |
| Gallery .. .. .     | 48.94 "                     |

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Boston, Mass., U.S.A.*

## NEUTRALITY.\*

By ALFRED H. ALLEN.

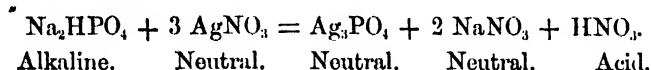
THE comparatively recent recognition of the true position of hydrogen has probably done much to retard the progress of chemical science, especially with respect to the theory of neutral salts. But perhaps still more injury has been done by the almost universal habit, which existed till a few years ago, of looking at the constitution of all saline compounds from the view of their action on litmus. One of the first things that a student was taught, and still is, in many cases, is that the criterion of normal constitution is neutrality to litmus. If the litmus is reddened the compound is "acid," or there is a "free acid" present; if reddened litmus is restored to blue there is an "alkali" present. I am not decrying the great value of the indications and teachings of litmus, if they are

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\* Abstract of a lecture delivered before the Chemists' Assistants' Association.



properly understood and interpreted, but merely pointing out the fallacy of relying implicitly on litmus as an indicator of chemical constitution. Thus, one may take two colourless liquids, one of which is without sensible effect on litmus, while the other turns reddened litmus to blue. On mixing the two the reaction will become strongly *acid*. Either we have converted an alkali into an acid, or the indicator is misleading us. The reaction which I have supposed to have occurred is this:—



Hence there was nitric acid formed by the reaction, which quite accounts for the reddening of the litmus.

Except in certain cases, litmus is a very uncertain indicator of constitution, but of the natural colouring matters it is undoubtedly the most generally available, and in certain cases it is still the best indicator of neutrality which can be used. The end-reaction is not readily observed by gaslight, but when daylight is not available the neutral point can be ascertained very sharply by employing the monochromatic light of an incandescent sodium compound (such as a bead of sodium carbonate held in a loop of platinum wire in a bunsen flame). By this light, an acid solution of litmus appears nearly colourless, while the blue solution looks almost black.

*Cochineal* may be advantageously used in some cases, as the change from yellowish-red with acids to purple with alkalis is sharply marked, and the indicator is not affected by carbonic acid. It gives an alkaline reaction with the carbonates of the alkaline-earth metals, and hence the so-called "temporary hardness" of water can be rapidly and accurately ascertained by titration with cochineal and standard acid. But, as pointed out by R. T. Thomson, a radical objection to its general employment is the fact that, in presence of very small quantities of iron or aluminium, the pink colour, though modified, persistently remains after the neutral point has been passed.

*Turmeric* is an indicator which has received but little application. Its chief advantage is the possibility of using it in an alcoholic solution. Its most curious reaction is that with boric acid, which turns litmus a wine-red, but behaves with turmeric much like a free alkali.

The progress of organic research has of late years enriched the laboratory with a number of indicators of neutrality, which may in many instances advantageously replace the formerly universally employed litmus.

The use of these indicators requires discretion, and the first thing the user is likely to discover is that they cannot be employed indiscriminately as a substitute for litmus. But this circumstance, which at first sight might appear to be an obstacle to their use, is, in reality, one of their great recommendations; for they often give sharp end-reactions where the indications of litmus are hopelessly indefinite.

The great majority of indicators of neutrality, including the colouring matter of

litmus, are bodies of an acid character, and they owe their value to the fact that the solutions of their alkali-metal salts have a colour distinctly different from that of the free acid or hydrogen salt. When the acid properties of the colouring matter are very feeble, or, in other words, when its "affinity" for bases is very weak, very feeble acids will displace it from its salts, with the characteristic change of colour indicating the liberation of the colour-acid. Such an indicator will be available for the titration of very feeble acids, and we have it in the invaluable colour-acid, *phenolphthalein*, a body which in solution in the free state is practically colourless, but the soluble metallic salts of which have, in solution, a magnificent crimson-red colour. By means of phenolphthalein and caustic alkali we can titrate very feeble acids, and either in aqueous or alcoholic solution, as may be preferred. With phenolphthalein, acetic, benzoic, citric, tartaric, and other organic acids, can be titrated far more accurately and sharply than with litmus; and it is equally available for stearic, oleic, and other insoluble fatty acids. In these latter cases, however, the operation should be conducted in alcoholic solution; not merely because the acids are insoluble in water, but because water effects more or less decomposition of their salts (soaps). Thus, on titrating an alcoholic solution of oleic acid with caustic soda the end-reaction is perfectly sharp; but on adding water a marked pink colour is developed, indicating that a certain amount of decomposition has taken place, probably owing to the partial hydrolysis of the soap with formation of an acid oleate and free caustic alkali.

Phenolphthalein is also available for the titration of many feeble mineral acids, including hydrocyanic, carbonic and arsenious acids, and even sulphuretted hydrogen. An interesting demonstration that phenolphthalein is affected by carbonic acid is obtained by adding that indicator to water rendered faintly alkaline by caustic soda. On then blowing through the liquid, it becomes decolorised by the carbonic acid of the breath. But the very fact that carbonic acid reacts on the indicator shows that the standard alkali used for a titration must be caustic and free from carbonate. This is very difficult to insure in the case of caustic potash and soda, and ammonia cannot be employed with phenolphthalein. By far the best standard alkaline solution for use with phenolphthalein is decinormal baryta water, which, if clear, must necessarily be free from carbonate.

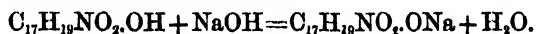
It may be set by any ordinary acid, but the compound to which I give the preference is the quadroxalate of potassium, a salt of the composition  $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4 + 2 \text{ aqua}$ . It is prepared by making a saturated solution of recrystallised oxalic acid in water and filtering the liquid. One-fourth of the filtrate is then heated to boiling, and neutralised with pure potassium bicarbonate, employing litmus paper as the indicator of neutrality. This neutralised portion is then added to the main quantity, whereupon there is copious deposition of the quadroxalate in the form of granular crystals. This is filtered off, washed with a little cold water, and dried over sulphuric acid. It is perfectly permanent in the air, and in that respect presents a great advantage over oxalic acid. In using the quadroxalate for setting the standard baryta solution, about 0.25 gramme is exactly weighed and dissolved in a little warm water. Phenolphthalein (1-500 solution in proof spirit) is

then added, and the baryta water run in until the pink colour becomes permanent. During the first part of the titration the solution remains quite clear, but subsequently a white precipitate of barium oxalate is produced, and this forms an extremely delicate background for viewing the end of the reaction. In fact, it is distinctly advantageous to aim at the presence of a finely-divided white precipitate in the liquid, rather than to employ a white background to the vessel. Potassium bitartrate may be substituted for the acid oxalate, but it is difficult to obtain the salt perfectly pure.

In many cases phenolphthalein can be advantageously employed with an ethereal solution of the acid to be determined. Thus, suppose it be desired to determine the benzoic acid in a sample of paregoric suspected not to be of B.P. quality. 20 c.c. may be taken, rendered slightly alkaline to litmus, the spirit evaporated off, and the camphor and oil of anise extracted by agitation with ether. On adding hydrochloric acid to the separated aqueous liquid, benzoic acid will be precipitated, and on agitation with ether will be extracted. The ethereal solution is separated, washed with small quantities of water till the washings no longer appreciably redden litmus, and placed in a small cylinder together with about 5 c.c. of water to which a drop of phenolphthalein solution has been added. On now dropping in  $\frac{N}{25}$  or  $\frac{N}{30}$  caustic soda or baryta, and agitating well between each addition, the estimation of the benzoic acid can be readily and accurately effected. The meconic acid of the opium is dissolved more or less completely by the ether used for extracting the benzoic acid, but the proportion present is too small to interfere with the determination of the latter.

The foregoing method of titrating benzoic acid also finds an application in the process of assaying aconite alkaloids suggested by me. By its means the proportion of saponifiable alkaloids in as little as half a grain of material can be ascertained with a considerable approach to accuracy. This is an important improvement in practice on the method based on the same principle originally proposed by Dr. Alder Wright, whose experiments were made prior to the utilisation of phenolphthalein as an indicator, and on such large quantities of material as to render the process quite prohibitive in actual practice.

But although phenolphthalein reacts perfectly with such weak acids as carbonic and hydrocyanic, there are bodies of an acid character which have little or no action on it. This is the case with phenol and other bodies of that class, such as morphine, the molecule of which contains a hydroxyl group having a phenolic function, which enables it to form compounds with the alkalies, and is the cause of its solubility in caustic alkalies and lime water. I lay some stress on the behaviour of morphine with phenolphthalein, because it has been stated that morphine reacts as an acid to phenolphthalein, until one molecular weight of NaHO has been added for each molecular weight of morphine; or, in other words, in the proportion for the reaction:—



In consequence of this statement, I have submitted the behaviour of morphine with phenolphthalein to direct experiment. The end-reaction is not a sharp one, and appears

to be modified by the presence of alcohol and other conditions, but in all cases I found the acidity of morphine to phenolphthaleïn extremely trifling, and the caustic alkali required for the production of a pink colour was only a small fraction of that which would be required for the above reaction.

P. C. Plugge (*Arch. Pharm.* 1[3] xxv., 45) finds also that in titrating morphine hydrochloride with caustic alkali and phenolphthaleïn a red coloration makes its appearance *before* the end of the reaction (that is the neutralisation of the HCl), but states that a little experience enables the difficulty to be overcome.

It is evident, therefore, that morphine has a faint acid tendency, but the statement that it reacted quantitatively as an acid to phenolphthaleïn was a mistake, and I think there is little doubt that the behaviour of morphine to phenolphthaleïn was confused with that to Poirrier's soluble blue CLB. This colouring matter, not now manufactured, was found by M. R. Engel in 1886 (*Compt. rend.*, cii., 214, 262, 431), to be capable of being used as an indicator for the very weakest acids.

The concentrated solutions of the compounds  $\text{KBO}_2$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{K}_3\text{AsO}_4$ ,  $\text{K}_2\text{PHO}_3$ ,  $\text{K}_2\text{PHO}_2$ , and  $\text{K}_2\text{CO}_3$ , are stated to have been found approximately neutral to this indicator. About 85 per cent. of the hydrogen of  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{AsO}_4$  was indicated, so that the colouring matter could not be used for the actual titration of these acids. It is only to be expected that the salts of very feeble acids should readily suffer hydrolysis, especially the salts in which the last atom of hydrogen is replaced. Morphine, phenol, resorcin, and chloral all reacted as acids to Poirrier's blue, the last three being capable of accurate titration by means of it. Phenol and chloral acted as monobasic, and resorcin as a dibasic acid. Morphine did not give such good results, a quantity of caustic alkali being required somewhat in excess (24 c.c. against 20), of that corresponding to "the double phenol function." The meaning of this is apparently that Engel found at least  $2\text{NaHO}$  to be required for  $\text{C}_{17}\text{H}_{20}\text{NO}_3$ . This result is interesting, but requires confirmation, as do other of Engel's observations. Engel found Poirrier's blue to be neutral to the hydroxyl group existing in monovalent alcohols (even when these were of tertiary constitution, like trimethylcarbinol and pinacone), but in strong solution polyvalent alcohols, such as glycerol, erythrol, and mannitol, showed an acid *tendency*, though they were not capable of being accurately titrated. Hydrocyanic acid could be determined by titration with Poirrier's blue, and glycocine, alanine and taurine also behaved as acids, but the end-reaction was indistinct.

It is interesting to observe that phenolphthaleïn and Poirrier's blue, which may be used as indicators for very feeble acids, are absolutely indifferent to the majority of the alkaloids and organic bases. Even aniline and pyridine, which have such strongly-marked basic characters, are perfectly neutral to phenolphthaleïn. The same is true of strychnine, quinine, aconitine, and, with the limitation already mentioned, morphine. Hence the salts of these bases, such as hydrochloride of aniline, sulphate of quinine, and nitrate of

aconitine\*, can be titrated with caustic alkali and phenolphthaleïn, just as if the respective acids were in an uncombined state. According to E. Léger, cicutine and codeine are exceptions to the general rule of indifference of the alkaloids to phenolphthaleïn, and, according to P. J. Plugge, nicotine and conine also exhibit an alkaline reaction. A curious exception to the general behaviour of alkaloids is also presented by atropine and its isomers (as also homatropine), which in the free state strongly redden phenolphthaleïn. This property, however, does not exist in alcoholic solution, a fact which marks a curious distinction between these alkaloids and the mineral alkalies, the alcoholic solutions of which react perfectly with phenolphthaleïn.

One inconvenience is attached to the use of phenolphthaleïn as an indicator, which is that it is gradually decomposed by ammonia, and hence cannot be safely used for titrating that base, or in presence of its salts; but this fact being recognised in practice, it causes very little inconvenience. Nevertheless, "an indicator possessing the general properties of phenolphthaleïn, but not possessing this imperfection, is still a desideratum."

But if phenolphthaleïn and its allies indicate very feeble acids, it is evident that they fail as indicators of the majority of alkaloids, and other of the feebler bases. If we desire an indicator for weak bases we must look for a substance which has a fairly strong affinity for bases, and which shows by a change of colour that it has "met its affinity." Of all indicators of the sort hitherto proposed, the one which best answers the required purposes is the azo-dye known as *helianthin* or *methyl-orange*. This colouring matter is the sodium salt of the sulphonic acid of dimethyl-amido-azobenzene. Its solutions have a yellow colour, but the free acid is red. Hence, the addition of an acid sufficiently powerful to liberate the acid from its salts results in a change of colour from yellow to red. This change is sufficiently marked, though it does not approach the sensitiveness of phenolphthaleïn to alkaloids, and is not available in a strongly alcoholic liquid. The free acid of methyl-orange, which for convenience may be termed "*helianthic acid*," is only sparingly soluble, but is none of the weakest in its affinities. Hence, feeble acids like boric, carbonic, and hydrocyanic are *wholly* unable to decompose its salts; acetic and oxalic acid do so only imperfectly; while with sulphuric, hydrochloric, nitric, and thiosulphuric acids, complete decomposition ensues. With phosphoric acid, decomposition ceases rigidly with the formation of a compound analogous to  $\text{Na}_2\text{HPO}_4$ , which fact has been utilised by Mr. J. Hodgkin for the examination of glacial phosphoric acid.

The soluble acid calcium phosphate, containing  $\text{CaH}_4(\text{PO}_4)_2$ , which is the leading constituent of commercial "superphosphates," is neutral to methyl-orange, and hence any excess of acid can be readily determined. The neutrality of these acid phosphates to methyl-orange is in striking contrast to the behaviour of the sodium phosphates with phenolphthaleïn, with which indicator  $\text{Na}_2\text{HPO}_4$  is neutral; while, according to Engel, with Poirrier's soluble blue, the compound  $\text{Na}_2\text{PO}_4$  is approximately indifferent.

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\*Ordinary nitrate of aconitine is not a neutral salt. It contains  $\text{B}_2(\text{HNO}_3)_2$ .

Methyl-orange being totally indifferent to such weak acids as boric, carbonic, sulphydric, and arsenious, the alkaline borates, carbonates, sulphides and arsenites behave just like their equivalents of free alkali. With methyl-orange as an indicator, standard acids may be set with sodium carbonate or borax (the latter salt having been actually recommended as giving a solution absolutely permanent and without action on glass); and the "temporary hardness" of water and the "total alkali" of soda ash may be determined in a few minutes. All the alkaloids and organic bases of which the behaviour has hitherto been examined—except urea, caffeine, theobromine, and, perhaps, aniline—may be titrated with methyl-orange and a standard mineral acid, and with much greater facility than when litmus is used (phenolphthaleïn, as already stated, is inapplicable).

An indicator which in every respect (except its non-destruction by nitrous acid) behaves like methyl-orange is the colouring matter inappropriately named *lacmoid*. In the form of paper, especially, this is a very useful indicator, which may be used in cases where the deep colour of the solution prohibits the employment of helianthin.

*(To be continued.)*

**The Determination of Sulphur in Coal by Eschka's method. F. Hundeshagen.** (*Chem. Zeit.*, xvi., 1070, 1071.)—Eschka's method for determining sulphur is liable to give low results from the loss of part of the sulphur as volatile compounds. Even when more than the prescribed quantity of the mixture of magnesia and sodium carbonate is used, as much as six per cent. of the total sulphur may be lost, and this amount may be much exceeded if the mixture be damp and the heating rapid. The volatilisation of a portion of the sulphur can easily be recognised by holding a strip of lead paper over the crucible.

The improvement advocated by the author consists in substituting potassium carbonate for the sodium salt. The mixture used by him is composed of two parts of magnesia, and one part of calcined potassium carbonate. Two parts of this are taken for one of coal. The reaction is quicker than with sodium carbonate, it being completed in a quarter or half-an-hour. The results quoted are about 0.15 per cent. higher with brown coals containing about 2 per cent. of sulphur. The reason for the low results with sodium carbonate is that it becomes anhydrous and comparatively inert at a somewhat low temperature, and, further, that sodium sulphide is easily decomposed by moist carbonic acid, the contrary, in each case, holding good for potassium carbonate. The absorption of sulphur is also facilitated by the formation of a certain quantity of potassium hydrate, under the conjoined influence of magnesia and moisture, there being but little tendency to form sodium hydrate under like conditions.

B. B.

**To Stain Bacteria in Fatty substances such as Milk.** (*Centralblatt f. Bakteriologie u. Parasiten Kunde*, xi. 10, through *Royal Microscopical Society's Journal*, 1892, p. 291) —A loopful of milk and a loopful of distilled water are mixed on a cover-glass, dried, and fixed at a gentle heat. The cover-glass is then placed in a watch-glass containing chloroform-methylene-blue (made by mixing 12 to 15 drops of a saturated alcoholic solution of methylene-blue and 3 to 4 c.c. of chloroform). In this solution the cover-glass is moved to and fro for 4 to 6 minutes. The chloroform is then allowed to evaporate, the preparation washed with, and examined in, water. In fresh milk and cream the bacteria only are stained, but, if curdled, the flakes of casein are dyed a pale blue. This does not, however, interfere with the distinctness of the bacteria, which are stained deep blue.

F. H. P. C.

**Estimation of Sulphuric Acid in Sulphates.** **A. v. Asboth.** (*Chem. Zeit.* 1892, xvi. 922.)—With reference to Stolle's method (*THE ANALYST*, xvii. 115), Asboth points out that a solution of barium chromate in hydrochloric acid begins to evolve chlorine very soon after it has been made, some of the barium chromate being, of course, simultaneously decomposed into barium and chromium chlorides. Such a solution was found to give very erroneous results, when used 24 hours after it had been made. If the barium chromate were dissolved in hydrochloric acid immediately before each determination, error might be avoided; but much of the convenience of the process would thus be sacrificed.

A. G. B.

**The Microscopic Examination of Butter by Polarised Light.** (*Collected from the original sources by H. D. Richmond.*)—The use of the microscope for detecting foreign fats in butter was first proposed by Hassal; it depends on the broad principle that fats, which have been fused and allowed to cool, contain crystals, which rotate somewhat a ray of polarized light, while butter fat does not. Campbell Brown (*Chem. News*, xxviii. 1), in 1873, and in 1874, Hohner and Angell, in "Butter and its Adulterations," dwelt upon this method, and give figures, showing the difference in appearance of pure and adulterated butter when microscopically examined by polarized light; Hohner and Angell, however, recognize the fact that pure butters sometimes give similar appearances to those of artificial samples. Mylius (*Ber.* xii. 270), in 1878, and Rabot (*Industrie Laitière*, 1885, No. 34, 271), in 1885, have discussed the method. The most complete memoir on the subject is by Taylor, who studied the subject from 1876 till 1885, presented to the Society of American Microscopists, at their Cleveland meeting in 1885. His results are scattered through the *Scientific American*, and the *Microscopic Journal*, during those years, and are collected in the *Industrie Laitière*, 1881, 47, 370, and the *Milch-Zeitung*, 1882, 2, 27, and 1885, 47, 744. Taylor is, on the whole, favourable to the method. Sell concludes (*Ueber Kunstbutter*, 63, *Berlin*, 1886), that there is not a specific difference between the crystals of butter and

those of beef fat, &c., on microscopic examination, because it is possible to produce conditions under which different kinds of fat behave in the same manner; he speaks highly of Taylor's work, from a scientific point of view, but denies to it a practical importance. Besana, in a recent work (*Sui metodi atti a distinguere il burro artificiale dal burro naturale*), attaches no importance to the microscopic examination of butter. Quite recently, Pouchet (*J. d'Agriculture pratique*, 1892, 1, 4), speaks highly of the method, the discovery of which he attributes to Penmetier, in 1888; his opinion has been widely published in English and French journals, both trade organs, and general periodicals. Pizzi (*Staz. Sper. Ag. Ital.* 1892, 131), has examined sundry genuine butters and margarines, and mixtures containing ten, five, and one per cent. of margarine; he publishes a plate, showing the appearance of these when examined with a selenite plate under polarized light, which shows that even  $1^\circ/\lambda$  gives faintly the characteristic colours of crystalline fats; he alleges that Sell (*loc. cit.*), does not state what are the conditions under which different kinds of fat behave in the same manner. Both Pouchet and Pizzi have done no more than establish the broad principle enounced by Hehner and Angell, as they do not appear to have examined any considerable number of butters. It is significant that Hehner, who may be regarded as one of the originators of the methods, has, in common with most other English analysts, discarded the method. At a recent meeting of the Society of Public Analysts, Stokes stated that he was always able to detect margarine by the microscope, while he not unfrequently found the same appearances in butter; he condemned the use of a selenite plate; his first statement was, however, doubted by Cassal and others.

The method adopted by all experimenters was practically the same, viz., to crush a small portion of the butter between two microscope slides, and to examine it with a low power ( $\frac{1}{2}$  to 1 inch), under polarized light; with pure butters, no definite change was visible; the presence of margarine or fused fats was shown by the light passing in certain portions of the field, giving a brilliant appearance, where no selenite plate was used, and a play of colours where it was introduced.

II. D. R.

**The Acetic Acid Test for Fats.** F. Jean. (*Industrie Laitière*, 1892. No. 26 205). The acetic acid used was glacial acetic acid, to which enough water had been added to raise the density to 1.0565 at 15°C.

Three c.c. of oil or fat are introduced into a tube 1 c.m. in diameter, and graduated in  $\frac{1}{10}$  of a c.c.; the tube is placed in a water bath at 50°C., and the volume of the fat accurately adjusted to 3 c.c. 3 c.c. of acetic acid, measured at a temperature of 22°C., are then poured in from a pipette. The fat and the acetic acid are shaken several times to ensure complete admixture, and the layers are allowed to separate completely in the water bath at 50°C. By subtracting the quantity of acetic acid from 3, and multiplying by 33.3, the percentage of acetic acid dissolved by the fat is obtained.



In this way numerous samples of butter of various sources were found to dissolve 63·33 per cent. acetic acid; 4 butters from Touraine however dissolved 73 per cent.

Maize, castor, cocoa-nut and mineral oils dissolved 100 per cent. of acetic acid; Indian poppy oil, 63·3; beech nut oil, 53·3; and camelina, nut, olive, *Arachis* (earth nut), neats foot, palm, sweet almond, poppy, radish, and rape oils, dissolved from 30 per cent. to 43·7 per cent.; margarine from 26·7 per cent. to 40 per cent; tallow, 26·7 per cent., and rosin oil nothing.

The author applies this test in conjunction with the reading of his oleorefractometer, and the Reichert-Wollny figure for the detection of adulteration in butter.

As examples of its use he gives figures.

| Description of Butters.     | Oleorefractometric Reading. | Solubility of Acetic Acid. | R.-W. Figure. |
|-----------------------------|-----------------------------|----------------------------|---------------|
| Normandy (pure) ..          | —30                         | 63·33                      | 29·25         |
| Rennes ( „ ) ..             | —29                         | 63·33                      | 27·5          |
| Touraine ( „ ) ..           | —36                         | 73·0                       | 31·42         |
| Brittany (suspicious) ..    | —25                         | 60·0                       | 24·7          |
| Ardennes (suspicious) ..    | —27                         | 58·33                      | —             |
| Indre-et-Loire (suspicious) | —26                         | 56·66                      | 25·75         |
| Rennes, salt (adulterated)  | —25                         | 60·0                       | 23·98         |
| „ (suspicious) ..           | —25                         | 60·0                       | —             |
| Brittany (suspicious) ..    | —25                         | 60·0                       | 22·99         |
| Rennes (suspicious) ..      | —26                         | 60·0                       | 22·0          |
| Brittany, salt (suspicious) | —25                         | 60·0                       | 23·65         |
| Isigny + 10 % cocoa-nut oil | —33                         | 66·66                      | 26·8          |
| „ + 15 % „ „                | —34 (strong)                | 90·0                       | —             |
| „ + 28 % „ „                | —36                         | 96·0                       | 24·13         |
| „ + margarine ..            | —24                         | 53·0                       | —             |

The author from these figures concludes that the three methods are enough to distinguish adulteration in butter, even with cocoa-nut oil. Thus the Isigny butter, adulterated with cocoa-nut oil, cannot be confounded with the Touraine butter, as though the oleorefractometric reading and the solubility of acetic acid increase, the Reichert-Wollny figure is lowered.

H. D. R.

**A Sensitive Reaction for Albumin in Urine.** By E. Spiegler. (*Ber.*, 1892, 25, 375—378). The urine is acidified with acetic acid, and cautiously dropped from a pipette into a solution of mercuric chloride (8 parts), tartaric acid (4 parts), and sugar (20 parts), in water (200 parts), when the presence of albumin is indicated by the formation of a sharp, white ring at the point of contact of the two liquids. The solution prepared as above has a specific gravity of 1·06; the sugar plays no part in the reaction, but is simply added to raise the density of the solution, and in testing strong diabetic

urines, a further addition of sugar is necessary to prevent its mixing with them. Peptone does not give the reaction, but propeptone does give it. One part of albumin in 150,000 is readily detected; whilst by allowing the test to stand for a few minutes, one part in 225,000 can be detected, whereas the sensitiveness of the ferrocyanide reaction has a limit of one part in 50,000.

A. R. L.

**The Purity of Olive Oil.** F. Lengfeld and L. Paparelli. (*Rev. Internat. des Falsificat.*, 1892, v., 98.)—The authors have examined certain samples of Californian olive oil, with the results given in the table below. Samples of a few other oils, namely, cotton seed and white and black mustard, were also tested.

|                   | No. of Oil. | Iodine Absorption. | Rise of Temp. deg. C. | Fatty Acids. per cent. | M.P. of Fatty Acids. deg. C. |
|-------------------|-------------|--------------------|-----------------------|------------------------|------------------------------|
| Californian.      | 1.          | 80.80              | 37                    | 94.5                   | Below 28                     |
|                   | 2.          | 77.28              | 35                    | 94.0                   | 28—30                        |
|                   | 3.          | 87.15              | 39.5                  | 96.05                  | Below 28                     |
|                   | 4.          | 83.35              | 37.5                  | 95.50                  | "                            |
|                   | 5.          | 88.68              | 41                    | 95.65                  | 28—30                        |
|                   | 6.          | 81.45              | 38                    | 95.93                  | Below 28                     |
|                   | 7.          | 79.50              | 36                    | 94.80                  | "                            |
|                   | 8.          | 79.53              | 34.5                  | 95.92                  | "                            |
|                   | 9.          | 78.42              | 33.5                  | 95.87                  | "                            |
|                   | 10.         | 78.45              | —                     | 95.68                  | "                            |
|                   | 11.         | 85.44              | 36.5                  | 95.98                  | "                            |
| Unknown origin.   | 12.         | 81.70              | 34                    | 95.77                  | Below 28                     |
|                   | 13.         | 81.50              | 35                    | 95.86                  | "                            |
|                   | 14.         | 78.52              | 34                    | 94.84                  | "                            |
|                   | 15.         | 78.51              | 33.5                  | 95.97                  | "                            |
|                   | 16.         | 105.40             | —                     | 96.59                  | 35—36                        |
| "Union Salad Oil" | 17.         | 105.30             | 72                    | 96.66                  | 35—36                        |
| Cotton-seed       | 18.         | 107.00             | 79                    | 96.17                  | 37—38                        |
| White Mustard     | 19.         | 97.68              | 49.5                  | 96.70                  | 34—36                        |
| Black Mustard     | 20.         | 103.07             | 58.5                  | —                      | 34—36                        |

The samples numbered from 1 to 11 inclusive were Californian olive oil, the purity of which the authors consider beyond question; those from 12 to 16 were of unknown origin. All the foregoing, with the exception of No. 16, gave no reaction with Bechi's, Hauche-corne's, or Brullé's reagents. No. 16 reacted with all three, as did also No. 17, which was sold under the title of Union Salad Oil. The sample of cotton-seed oil gave a reaction in each case, while the two samples of mustard oil gave no reaction with the Bechi test, but were detected by the other two reagents.

B. B.

**Analysis of Sulphides.** P. Jannasch, V. Wasowicz, K. Aschoff, and T. Bickes (*Jour. f. Prakt. Chem.*, 1892, XLV., 94-114.)

(1.) *Molybdenum Glance*.—The finely-powdered mineral is heated in a platinum boat in a combustion tube through which a current of oxygen is passed. The temperature is kept low at first and gradually raised, but must not be sufficiently high to volatilise molybdic acid. The evolved vapour of "sulphuric acid" and sulphurous anhydride are absorbed in a 3 per cent. solution of hydrogen dioxide. When the colour of the contents of the boat have passed to a greyish white, with perhaps a greenish tinge, the decomposition is complete, and the boat is withdrawn. The tube is washed with hot water and the washings added to the hydrogen dioxide in the absorption vessels. The mixed liquids are evaporated to 100 c.c., acidified with hydrochloric acid, and precipitated with barium chloride, with the usual precautions, for estimation of the sulphuric acid. To determine the molybdic acid, the boat, with its contents, is weighed, and the latter dissolved in ammonia, when as a rule a gangue, consisting of a reddish powder, remains undissolved. This is filtered off, washed with ammonia, and treated with hydrochloric acid for the determination of iron and silica by the usual methods. The ammoniacal solution is evaporated until all free ammonia has been expelled and precipitated with a solution of mercurous nitrate. After 24 hours the precipitate is filtered, washed with a dilute solution of mercurous nitrate, dried at 110°, and removed as far as possible from the filter into a Rose's crucible, that which adheres to the filter being dissolved in dilute nitric acid and added to the crucible, from which the liquid is then evaporated on the water-bath. The mercurous molybdate is finally reduced in hydrogen, at first over an ordinary gas flame and finally over the blow-pipe, and the molybdenum weighed. Two hours heating is frequently necessary before the weight is constant.

(2.) *Realgar and Orpiment*.—The decomposition is effected as in the case of molybdenum glance, but all the arsenic passes into the absorption vessels. The gangue can thus be weighed directly, as the residue in the boat. The hydrogen dioxide solution is concentrated to about 140 c.c., excess of ammonia is added, followed, when the liquid is cold, by magnesia mixture, made with magnesium chloride, a large excess being avoided. After 24 hours the precipitate is filtered, washed with ammonia, dissolved in hydrochloric acid, and again precipitated with ammonia and another drop or two of magnesia mixture. The ppt. is finally dried at 100°, and transferred to a Rose's crucible, that adhering to the paper being dissolved in dilute nitric acid, added to the crucible, and the liquid evaporated. Finally the crucible is heated at a gradually increasing temperature to redness, a current of oxygen being passed the while. The sulphuric acid is determined in the original filtrate from the ammonium magnesium arsenate after evaporating off the ammonia and acidifying with hydrochloric acid.

(3.) *Galena*.—The powdered sample is heated to dark redness in a boat in a combustion tube, through which a stream of oxygen carrying nitric acid vapour (which has been taken up by the oxygen in bubbling through fuming nitric acid) is passed. Hydrogen

dioxide is again used as the absorbent. After an hour a saturated solution of ammonium carbonate, kept warm and containing undissolved ammonium carbonate, and air are substituted for the nitric acid and oxygen respectively; the temperature of the tube is once more raised to redness and kept there until the contents of the boat have become a bright yellow liquid consisting of molten lead oxide, which generally happens in half an hour. The boat is withdrawn from the cooled tube, and the latter is washed with hot water, the washings being mixed with the absorbing liquid. The sulphuric acid is determined in the mixed liquids in the usual way. The lead oxide is dissolved from the boat in nitric acid, and determined as usual, if required. Air has to be substituted for oxygen when ammonium carbonate is used, to avoid explosions.

The authors have devised other methods for analysing galena in the wet way. The mineral is oxidised with strong nitric acid, any separated sulphur being oxidised by the addition of bromine; the mass is evaporated to dryness and, lest any lead bromate be formed, moistened with strong hydrochloric acid, and again evaporated three or four times. The lead sulphate is then dissolved in sodium hydroxide, filtered from gangue, and the lead precipitated from the solution as peroxide, either by chlorine or bromine, in the cold; or the lead sulphate may be dissolved in ammoniacal ammonium acetate, and precipitated by hydrogen dioxide in the cold. The lead peroxide may be dissolved in nitric acid after the addition of a little alcohol, and the lead weighed as sulphate. The sulphuric acid is determined in the filtrate from the peroxide.

The authors also find that it is possible to determine the sulphur and lead in galena by heating the mineral in a stream of air laden with bromine vapour. The sulphur passes on, apparently, as sulphur bromide, and the lead remains as lead bromide, which is non-volatile at the temperature necessary, namely, the melting point of the bromide.

A. G. B.

**The Occurrence of Metallic Lead in Tartaric Acid.** Guillet. (*J. Pharm. Chim.*, 1892, xxv., 541, through *Chem. Zeit.*)—The author has found lead in samples of tartaric acid intended for pharmaceutical use. (See preceding Abstract.) Such tartaric acid did not wholly dissolve in 90% alcohol, nor in water, and contained 0.514% of ash. The aqueous solution of the acid, when saturated with ammonia and made feebly acid with hydrochloric acid, gave a precipitate of lead sulphide with sulphuretted hydrogen. 0.0528 gm. of lead was obtained from the solution of 1 kilo of the acid. The residue left on dissolving 1 kilo of the acid in boiling water, consisted of fragments of wood, crystals of calcium sulphate and metallic lead. The latter were picked out by hand and weighed; the quantity was 0.0626 grms. The lead is derived from the wooden lead-lined vessels used in the manufacture of the acid.

B. B.

**Lead in Tartaric Acid.** C. Buchel. (*J. Pharm. Chem.*, 1892, xxv., 540, through *Chem. Zeit.*)—The author has found combined and even free lead in all the samples of tartaric acid, both of French and foreign make, that he has examined. B. B.

**The Impossibility of completely separating Barium as Sulphate from strong solutions of Strontium Salts.** S. Cannepin. (*L'Union Pharm.*, through *Chem. Zeit.*)—The author finds, in spite of the statements to the contrary of Barthe and Falières, that it is impossible to separate barium completely as sulphate from concentrated solutions of strontium salts, as there is a limit to the re-action, beyond which the precipitated barium sulphate gives up as much barium to the strontium solution as the calcium sulphate or strontium sulphate, used as a precipitant, throws down. Complete separation can be effected by the use of strontium chromate, for which potassium bichromate may be conveniently substituted, provided the presence of potassium be unobjectionable.

B. B.

**Hübl's Iodine Absorption Method.** D. Holde. (*Chem. Zeit.*, 1892, XVI., 1176—1178.)—The author has stated in previous communications that the Hübl method, as usually carried out, does not give the highest or concordant results. He has come to the conclusion that for most of the oils he has examined, an excess of 65 to 75 per cent. of iodine is necessary, and that the iodine solution should be freshly prepared. Some time after the publication of these precautions, Fahrion published some improvements of the method, in which the author's suggested large excess of iodine was adopted, and the plan of keeping the solutions of mercuric chloride and iodine separate recommended. Although economical, this plan should, according to Benedikt, with whom the author concurs, be modified by mixing the solutions at least two days before use, as the alteration in strength of the solution immediately after mixing is apt to be great. The differences due to variations in the method of standardising the iodine solution are shown by the following example: 0.2 gram of an oil with an iodine absorption of 100 was dissolved in chloroform in the usual way, 50 c.c. of an iodine solution, two days old, added, and the reaction allowed to proceed for two hours. Two blanks were used, one at the beginning, the other at the end of the period of absorption. According to the former the amount of iodine present was 1.008 gramme, while the latter gave 1.000 gramme, and the titration of the oil showed that 0.800 gramme of iodine remained unabsorbed. According to the former method, therefore, the oil absorbed 0.208 gramme of I., that is, it had an iodine absorption of 104, while taking the latter figure, it absorbed 0.200 gramme, and its iodine absorption was therefore 100. Strictly speaking, the value, 1.000 gramme, got by the end titration is somewhat too low, as a part of the iodine would have been absorbed by the oil before it has ceased to be free and active by spontaneous loss of strength of the Hübl solution, so that the real correction may be taken as 0.007 instead of 0.008 gramme. Practically however, this makes little difference, the figure becoming 100.5 instead of 100, provided that the excess of iodine used be so large that the quantity remaining free throughout the operation is comparable with the total amount contained in the blank.

The difference between the values got by standardising the Hübl solution at the beginning and end of the operation is less than given above, when the solution is more than two days old, and therefore, alters in strength correspondingly more slowly.

It may be said, for the sake of clearness, that the author and Benedikt reckon the excess of iodine prescribed on the total amount contained in the quantity of solution used either for the blank or for adding to the oil, while Fahrion refers his percentage to the amount of iodine absorbed by the oil. Thus an excess 50 per cent in the phraseology of the former is equal to 100 per cent. in that of the latter.

The considerable variations that may arise from using too small an excess of iodine and the differences displayed in this respect by different oils, are exhibited in the following table :—

| Kind of oil and<br>Solution used.     | No. of C.C.'s of<br>Iodine solution. | Excess of Iodine<br>calculated on<br>total iodine<br>used. | Iodine<br>number |
|---------------------------------------|--------------------------------------|--|------------------|
| Linseed oil (1) (weak<br>I solution)  | 30                                   | 50 per cent.   | 158·8            |
|                                       | 40                                   | 58 „   | 164·8            |
|                                       | 50                                   | 65 „   | 169·4            |
|                                       | 60                                   | 70 „   | 172·1            |
|                                       | 70                                   | 76 „   | 173·0            |
| Linseed oil (1) (fresh<br>I solution) | 80                                   | 78·1 „   | 173·1            |
|                                       | 30                                   | 58 „   | 167·2            |
|                                       | 40                                   | 66 „   | 171·2            |
|                                       | 60                                   | 78 „   | 175·1            |
|                                       | 70                                   | 81 „   | 175·1            |
| Walnut (1) (fresh<br>I solution)      | 80                                   | 83 „   | 174·4            |
|                                       | 20                                   | 50 „   | 136·5            |
|                                       | 25                                   | 60 „   | 135·3            |
|                                       | 40                                   | 74 „   | 136·2            |
|                                       | 17                                   | 44 „   | 97·6             |
| Rape oil (1)                          | 20                                   | 57 „   | 98·8             |
|                                       | 35                                   | 78 „   | 99·7             |
|                                       | 45                                   | 82 „   | 100·3            |
|                                       | 55                                   | 84 „   | 100·3            |

With linseed oil and rape oil an excess of 75 per cent. of iodine is, therefore, necessary. With walnut oil a smaller excess suffices.

The author, in conclusion, insists on the necessity of observing other precautions such as exactitude of reading the burette and measuring the Hübl solution, for which he appears to use a burette. In the case of titrating a large number of samples he makes a blank experiment at the beginning and end of the titration, and calculates therefrom the exact value of the solution at the moment each sample is being titrated. B. B.

(NOTE BY ABSTRACTOR.—The majority of the author's difficulties and the manifold devices to which he has been driven to circumvent them, appear to arise from the short time allowed for the absorption (two hours), which should be at least trebled to insure the completion of the reaction.)

# THE ANALYST.

NOVEMBER, 1892.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE first Meeting of the Session was held at the Rooms of the Society of Arts, John Street, Adelphi, on Wednesday, 5th October. The chair was occupied by the President (Mr. O. Hehner).

The minutes of the last meeting were read and confirmed.

The following gentlemen were duly elected Members of the Society:—Messrs. Gustavo Antonio Abrines, E. J. Bevan, and John Bate Nickolls.

Dr. Sykes temporarily occupied the chair during the reading and discussion of the following paper:—

### ON THE INFLUENCE OF ALUMED BAKING POWDER ON PEPTIC DIGESTION, WITH REMARKS ON A RECENT PROSECUTION.

BY OTTO HEHNER.

It is well known to public analysts that in 1880 the Recorder of Cambridge decided that baking powder could not be considered an article of food, and did not, therefore, come within the scope of the Sale of Food and Drugs Act, and that, even if it did, the presence of alum in baking powder did not render it injurious to health. In consequence of this decision, alumed baking powder has ever since been freely and extensively sold throughout the country.

All public analysts being agreed to regard alum in bread as an adulteration, and alumed bread having, in consequence, practically disappeared, the decision of the above-mentioned Recorder has always appeared to me, as no doubt to most of my colleagues, to be both illogical and absurd, as well as detrimental to the interests of the consumers. Knowing that in the Midlands especially the sale of alumed baking powder was very common, I brought the matter before one of the County Councils for which I act as public analyst, and received their sanction to bring a case into Court, in the hope of obtaining a reversal of the Cambridge decision.

Among several samples of baking powder submitted to me for analysis was one which gave the following analytical results:—

|                     |     |     |     |             |           |
|---------------------|-----|-----|-----|-------------|-----------|
| Alumina             | ... | ... | ... | 4.97        | per cent. |
| Carbonic acid       | ... | ... | ... | 9.76 & 9.85 | „         |
| Sulphuric acid      | ... | ... | ... | 15.13       | „         |
| Ammonia             | ... | ... | ... | 0.12        | „         |
| Starch              | ... | ... | ... | 33.40       | „         |
| Residue on ignition | ... | ... | ... | 31.11       | „         |

From these figures the composition of the baking powder was calculated to be as follows:—4.97 per cent. of alumina correspond to 45.80 per cent. of crystallised potash alum, while 15.13 per cent. of sulphuric acid equals 44.58 per cent. alum. The carbonic acid corresponds to 18.63 and 18.80 per cent. of sodium bicarbonate. Subtracting from the ash the anhydrous alum calculated from the amount of crystallised alum (24.96), there is left 6.15 per cent. of soda, equal to 16.66 per cent. of bicarbonate, a figure approximating sufficiently near to the amount calculated from the carbonic acid determination. Thus the entire composition of the powder was:—

|                             |     |     |     |     |       |
|-----------------------------|-----|-----|-----|-----|-------|
| Crystallised alum           | ... | ... | ... | ... | 45.80 |
| Bicarbonate of soda         | ... | ... | ... | ... | 18.71 |
| Starch                      | ... | ... | ... | ... | 33.40 |
| Moisture and not determined | ... | ... | ... | ... | 2.08  |

100.00

Nearly one-half of the sample consisted, therefore, of alum, while the article upon which the prosecution in 1880 was based contained but 29 per cent. of crystallised alum.

On Feb. 18th, 1880 (ANALYST, vol. v., p. 67), Mr. West Knights brought a number of experiments before this society, which showed in a marked manner the profound influence of alum in artificial digestions of bread and flour, but inasmuch as I expected that it would be argued, as indeed it was at the hearing of the case, that alum was quite a different thing to alumed baking powder, and that in the latter the alumina was rendered insoluble by precipitation with sodium bicarbonate, I undertook a number of experiments with alum, as well as with alumed baking powder, to test this matter, and the results of this research I propose now to lay before you.

Theoretically, one equivalent of alum should require for complete precipitation six equivalents of sodium bicarbonate, or 948 parts of alum, 504 parts of sodium bicarbonate. The 18.71 parts of sodium bicarbonate contained in the sample should be able to precipitate 35.19 parts of alum, while 45.80 were actually present. It should be expected, therefore, that when the baking powder in question had been mixed with water, after the completion of the reaction a considerable amount of alumina would be left in solution as



alum. I found, however, while there certainly was a marked trace of alumina left in solution, its quantity was less than is required by theory. No doubt the reaction is somewhat more complicated than might at first be expected, not only pure hydrated alumina but also basic alumina salts being precipitated, thus giving the bicarbonate a somewhat greater precipitating power than would correspond to the above proportions. In any case, we have to deal with precipitated alumina hydrate, with basic sulphate of alumina, and with some soluble salt of the base.

According to the directions on the wrapper furnished me, in which the sample had been sold, a heaped teaspoonful of the powder was recommended to be used to every pound of flour. I found the weight of an ordinary teaspoonful to be, on an average of six weighings, 11.21 grammes. Assuming that two pounds of flour furnish three pounds of bread, a four-pound loaf of bread made in the manner directed on the wrapper would contain no less than 210 grains of alum.

*Experiments on the Digestion of Egg-albumen.*

A solution of pepsin was made, containing 0.02 gramme of pepsin in 100 c.c. of water. It had previously been ascertained that the pepsine in question was very active and was capable of digesting, under favourable conditions, 2,500 times its weight of hard-boiled white of egg, at 50° C., in about three to four hours. 5 c.c. of the pepsin solution contained, therefore, one milligramme of pepsin and was able to dissolve 2.5 grammes of white of egg in a fluid containing 0.2 per cent. of hydrochloric acid. In a few preliminary blank experiments this was found to be the case, while in the presence of baking powder, in proportion equal to that recommended by the manufacturer, a considerable quantity of albumen could not be brought into solution; a similar residue was observed when alum itself, to the extent of one-half of the quantity of baking-powder, was added in another trial. Quantitative experiments were then made.

Experiment 1.—Two grammes of hard-boiled white of egg and 0.05 gramme of baking powder were digested with one milligramme of pepsin for five hours. The residue left was washed with a little cold water, and the insoluble nitrogen determined by Kjeldahl's process. 0.0407 gramme of dry albumen, corresponding to 0.28 of fresh white of egg (with 85.5 per cent of moisture), or 14 per cent. of the amount taken, was found insoluble.

Experiment 2.—A precisely similar experiment was made, only instead of baking powder the corresponding amount of crystallised alum (0.025 gramme) was taken. Left insoluble 0.0402 dry albumen, or 13.8 per cent. of the amount taken.

Experiments 3 and 4.—In two other similar experiments with the same proportion of baking powder and alum as before, 0.0812 and 0.0743 dry albumen were left, corresponding to 28.0 and 25.6 per cent. of the wet albumen taken.

Experiments 5 and 6.—In these the quantity of baking powder and alum taken was increased four-fold, namely, to 0·2 and 0·1 gramme for 2 grammes of white of egg respectively. There were left, after six hours' digestion, 46·7 and 39·2 per cent. of the albumen taken.

Experiment 7.—This was a repeat experiment, with 0·1 gramme of alum for 2 grammes of white of egg. After 6 hours there were left 52·7 per cent of undigested white of egg.

It is seen that on repetition closely corresponding results could not be obtained, for although the egg had been rubbed through a very fine wire sieve, it was apt to cake together with the formation of little lumps, which could not be easily separated by shaking. But, speaking generally, the results show that the same quantities of alum, either taken pure or in the form of baking powder, prevent to an equal extent the digestion of hard-boiled white of egg. Parallel with every set of trials a blank experiment was made, without alum or baking powder, and the white of egg was in every case completely dissolved. As far as egg-digestion, therefore, is concerned, alumed baking powder is quite as injurious as alum itself.

#### *Experiments on the Digestion of Wheat Flour.*

Wheat-flour, containing 1·73 per cent. of nitrogen, corresponding to 10·81 per cent. of albuminoids, was similarly digested. In a blank experiment, without alum or baking powder, there was left undissolved after six hours' digestion of two grammes, 0·0280 gramme of albumen, or 12·9 per cent. of the albuminoids.

Experiment 8.—In the presence of 0·05 gramme of baking powder, with (nearly) 0·025 gramme of alum, there was left undissolved after six hours 0·0318 gramme, or 14·9 per cent.

Experiment 9.—When the amount of baking powder added was fourfold, namely 0·2 gramme, the same percentage of albuminoids was left undissolved, 0·0318 gramme, or 14·9 per cent. remaining.

Experiment 10.—With an amount of alum corresponding to 0·05 gramme of baking powder, viz., 0·025 gramme alum, there remained after six hours a residue of albuminoid of 0·0743 gramme, or 34·4 per cent. of the total amount taken.

Experiment 11.—With the fourfold amount of alum there remained 0·1187 gramme, or 54·9 per cent.

In the case of digestion of flour, therefore, alumed baking powder has far less influence than the corresponding amount of alum contained in it. Alum itself has a most injurious influence upon the digestion of flour, while that of alumed baking powder is slight.

*Experiments with Bread.*

Experiment 12.—Two grammes of the crumb of bread free from alum were digested as before. The residue left after six hours was Kjeldahled and found to contain nitrogen corresponding to 0.0231 gramme albuminoids. Unfortunately, the percentage of nitrogen in the bread itself was not determined; hence the results in the following experiments can only be judged by comparison, but no great error can be committed if it be assumed that the bread contained 7 per cent. of albuminoids, which is the mean given by Koenig in his vast collection of analytical results. In this case 16.5 per cent. of the total were left undissolved.

Experiment 13.—Two grammes of the bread-crumbs, digested with 0.05 gramme baking powder, left 0.0315 gramme albuminoids undigested; or, calling the amount left in the blank 100, there were left 136.3, or 22.5 per cent of the amount taken.

Experiment 14.—With 0.2 gramme of baking powder there remained undissolved 0.0407 gramme albuminoids, or 172.6 per cent. in comparison with the blank, or 29.1 per cent. of the original amount taken.

Experiments 15 and 16.—In corresponding experiments with alum only, namely, 0.025 and 0.1 gramme, there were left 0.0315 and 0.0516 gramme. These figures correspond respectively to 136.3 and 223.4, compared with the blank, or to 22.5 and 36.9 per cent. of the total albumen taken.

Curiously, therefore, the influence of baking powder containing alum upon the digestion of bread is more marked than in the case of the raw flour. With small amounts, or rather the amount of baking powder recommended to be taken by the manufacturer, the influence of alum and of alumed baking powder is equal, but with larger quantities the alum acts more detrimentally than does the baking powder.

*Experiments with Milk.*

Experiment 15.—5 c.c. of milk were digested for six hours without the addition of either alum or baking powder. There were left insoluble 0.0465 gramme of albuminoids. In this case also the total amount of albuminoid in the milk had not been estimated, but taking 3.66 to be the average of albuminoids in genuine milk, there was left 63.5 per cent. of the total nitrogenous matter taken.

Experiment 16.—5 c.c. of the same milk, digested with 0.05 gramme of baking powder, left 0.0681 grammes of albuminoids, or, calling the amount left in the blank experiment 100, there remained 146.5, or 93 per cent. of the amount of albuminoids taken.

Experiment 17.—Adding the fourfold quantity of alumed baking powder, there were obtained exactly similar figures, namely, 0.0681 gramme, or 146.5 compared with the blank, or 93.0 per cent. of the total taken.

Experiments 18 and 19.—Using the corresponding amount of crystallised alum, namely, 0.025 and 0.1 gramme, there were left in each case 0.0562 gramme of nitrogenous matter undigested, or, compared with the blank as 100 to 121 parts, or 76.7 per cent. of the amount taken.

It is remarkable that in the digestion of milk the alumed baking powder exerts a more injurious influence than does the amount of alum contained in it, and the smaller amount of alum, whether taken as baking powder or as crystallised alum, acts as markedly as does the four times larger quantity.

Experiments 20, 21, and 22.—In order to ascertain whether baking powder free from alum had any retarding influence upon digestion, three trials were made :—A blank digestion of hard-boiled white of egg, without baking powder ; a similar experiment with the addition of 0.05 gramme of alum-free baking powder, and a third with 0.2 gramme of the same baking powder. In all three cases the whole of the white of egg dissolved in five hours, nothing insoluble being left.

It is evident that in the digestion of egg, at least, alum-free baking powder is without detrimental influence.

#### *Physiological Experiments.*

I weighed out four quantities of alumed baking powder, amounting to two grammes. This is very nearly the quantity which would be contained in four ounces of bread, if made according to the directions on the label (the exact amount would be 1.88 grammes), mixed them with water, waiting until the effervescence had finished, added some sugar to render the dose palatable, and took one dose myself, giving the other three to my assistants. I requested them to let me know next morning their symptoms, without previous communication with each other. We were all in perfect health before taking the dose. Already, about an hour-and-a-half afterwards, unpleasant symptoms began to appear. Speaking for myself, I experienced first a feeling of great weight in the region of the stomach, later on pains in the epigastric region, slight difficulty in breathing, headache, and ultimately slight diarrhoea,—symptoms resembling an attack of indigestion. My assistants were similarly affected, and felt discomfort for several days.

After complete recovery, I took in a similar manner one gramme of the powder, or a quantity which would be contained in as little as two ounces of bread. Similar symptoms, almost to an equal degree, manifested themselves.

I have, therefore, come to the following conclusion :—that alumed baking powder exerts a most injurious influence upon digestion, whether artificial or within the body ; that the presence of alum in baking powder must be regarded as an adulteration injurious to health ; that samples containing alum should be condemned as injurious, even though magistrates and recorders declare alum to be quite harmless ; and that the sodium

bicarbonate contained in the baking powder does not neutralise the objectionable qualities of the alum. This, indeed, was not to be expected upon chemical grounds, inasmuch as the precipitated hydrate of alumina is readily soluble in dilute acid, and in the baking of bread the temperature does not rise in the interior of the loaf to anything like the point at which hydrate of alumina loses its water of constitution.

At the hearing of the case in question certain evidence was given for the defence, to which I will shortly refer. Mr. Wynter Blyth, who in his work on "Foods" declared "there can be no difference of opinion that it (alum in bread) is a serious adulteration, and not to be permitted," and who has, in his capacity as public analyst, condemned samples of bread containing alum as adulterated, came forward on behalf of the manufacturers of this baking powder, and stated that he considered alum in bread to be an entirely different thing to alum in baking powder; and that he had for some time past used in his household bread made with the baking powder in question without experiencing any injurious effects. Mr. F. Sutton, public analyst, who, as far back as 1872, had given a testimonial to the identical maker of this baking powder, in which it was lauded in the strongest language, went further, and attributed to alumed baking powder the valuable property of fattening pigs, if added to their ordinary food. He would continue to condemn alum in bread, but would not object to alumed baking powder. Dr. Thudichum, who, not being a public analyst, felt himself still freer from restraint, strongly stated that he considered alum itself to be possessed of valuable digestive properties. No attempt was made on the part of these three gentlemen to rebut the digestion experiments which I laid before the Bench, as I now lay them before you to-night, only the general statement being made that natural gastric juice was an altogether different thing from the artificially prepared article; and that as to my personal feelings and those of my assistants, all that could be urged was that we must have persuaded ourselves we were ill when all the time in reality we were perfectly well.

The magistrates, in view of this conflict of evidence, which certainly was quite unreconcilable, dismissed the case upon the same grounds as those enunciated by the Recorder of Cambridge.

I trust that my present contribution to the subject will go some way towards advancing the matter to a final and more satisfactory settlement. It is clearly my opinion<sup>1</sup> that as public analysts we should be acting contrary to public interests if we passed alumed baking powder as a genuine and legitimate article.

My best thanks are due to my assistant, Mr. W. P. Skertchly, for carrying out the analytical work involved in this investigation.

#### DISCUSSION.

The Chairman, in inviting discussion, said he felt sure that the members present had all listened with much interest to the paper just read. Mr. Hehner had gone into

the experimental side of the question very fully, and he (the chairman) thought that the strong evidence as to the deleterious action of alumina on the human economy which had been brought before them that evening, could not fail to convince any unbiased mind that its presence in baking powder was highly undesirable.

Mr. Cassal thought it desirable that by some expression of opinion on the part of the members of the Society the president should be supported in his position in the baking powder case under notice, of which, of course, they had all heard. It was extremely unfortunate that prominent public analysts should appear in Court and should give evidence against one another—especially evidence of the kind they had heard about, and he was exceedingly surprised at the statements which Mr. Wynter Blyth and Dr. Thudichum made in the case. It was equally regrettable that Mr. Sutton, who was a well-known public analyst, should have given the evidence that he was reported to have given. He (Mr. Cassal) gathered from what the president had said that hydrate of alumina was to be regarded as, in a sense, equally injurious with alum, and as, in fact, *the* injurious substance which might be present in bread that had been made from alumed baking powder. The contention of Messrs. Blyth and Sutton appeared to be that alum, as alum, was the only thing that could be injurious in bread or flour. It was very important that the president's experiments should be made known, as far as possible, among public analysts, inasmuch as they appeared to show that hydrate of alumina was in itself a distinctly injurious substance. That at once disposed of the only argument that Messrs. Blyth and Sutton had, namely, that carbonate of soda having precipitated hydrate of alumina, alum could no longer be present as such, and, therefore, that there could be no injury to the health of the consumer. It must be plain to the society that if the magistrates had properly appreciated the weight of the evidence before them, they ought to have given their decision in favour of the County Council. It was plain enough that they had definite scientific experiments on the one side, and mere assertions, of little or no scientific value, on the other. He therefore felt that the meeting would be perfectly justified in supporting the president of the Society, and in expressing their regret that two prominent public analysts—and two prominent members of the Society—should have given the evidence that they had given on that occasion.

Mr. H. Droop Richmond said it appeared to him that the president's experiments were hardly as conclusive as might have been wished. For instance, the experiments which he had made, and in which he and his assistants had swallowed alumed baking powder, were not, to his mind, conclusive. When given in that form it was concentrated, but if the same quantity were put into bread, it was spread over a much larger surface, and consequently only a small quantity of the alum was exposed to the action of the pepsin in the stomach. He believed that if the experiments were repeated, and if the president and his three assistants ate four ounces of bread containing the baking powder, the experiments would be more conclusive. He thought that in the case of bread, the peptic

digestion only played a small part in the total digestion. Pepsin had no amylolytic function, and the starchy portion would protect the remainder from attack during the short time it remained in the stomach; he believed that the pancreatic digestion played the more important part. He hoped that if the president were going to make any more experiments, he would try them with pancreatic extract, and see if there was the same retarding effect there. He did not wish it to be inferred, in suggesting to the president that he should make other experiments, that the experiments already carried out were not worth anything, because he thought they were extremely valuable, but he did not think they had gone as far as they could have been pushed.

The President felt bound to say, in reply to Mr. Richmond's remarks, that he thought, given plenty of gastric or pancreatic juice, the food might have been digested in spite of the alum. Probably individuals in very good health, and blessed with excellent digestions, might be able to digest bread even if it contained alum. What he did wish to lay particular stress upon was, that an article which, when taken in a moderate quantity and diluted with water, was injurious, should not be used in food. Of course, the injurious effects might be minimised in the case of a healthy person.

Mr. Cassal asked whether the case was appealed against, or whether there was any question of appealing? He supposed the usual excuse was made that a decision had been given on a question of fact and not of law.

The President replied that the County Council came to the conclusion that it was no use appealing, since evidence similar to that given at Ilkeston would certainly be brought forward again; and in view of a direct conflict of evidence an appeal would probably fail.

Mr. Cassal pointed out that the decision of the Recorder of Cambridge, or the decision of a magistrate, did not make law, and had really no weight at all; and he would take the opportunity of suggesting that whenever possible these gentlemen should be set right as far as was practicable. He thought it a very excellent thing to do in the interests of the public. Moreover, the very unfortunate circumstances which the President deplored, were only brought out on occasions of that kind, and they could hardly hope for the reforms required, unless the evil was clearly before the members of the profession.

The President wished to add that the case referred to was not finally decided and could be taken up again at any time. He had brought these experiments forward in order gradually to accumulate matter for such a contingency.

The President then resumed the Chair, and Mr. Skertchly read the following paper:—

#### NOTES ON W. F. K. STOCK'S NITROGEN PROCESS.

By W. PEARSON SKERTCHLY.

IN THE ANALYST, vol. xvii., No. 194, appeared a paper by Mr. W. F. K. Stock on a "New and Rapid Method for the Determination of Nitrogen in Organic Bodies." The process

is based upon the oxidation of the substance by a mixture of strong sulphuric acid and manganese dioxide. This paper was read before a meeting of the members of the Society in May last, and, from the discussion which followed the reading of the paper, it appears that several members cast considerable doubt on the accuracy of the method, fearing that the use of manganese dioxide would cause considerable error in the estimation of the nitrogen.

Mr. Stock wrote a supplementary paper (*THE ANALYST*, xvii., 196), to prove that there was not the slightest danger of losing any nitrogen if the process was properly carried out.

I have also made a series of experiments to test the efficacy of the method, both with pure ammonia salts and with various nitrogenous organic substances. The figures that I obtained in my analyses I now wish to bring before you.

A solution of crystallized ammonium sulphate was made up, and two separate distillations gave 0.15895 grm. and 0.15810 grm. as the ammonia ( $\text{NH}_3$ ) contents of 20 c.c. of this solution.

20 c.c. of the solution were now evaporated to dryness, with the addition of a few drops of dilute sulphuric acid, and treated with 10 c.c. of strong sulphuric acid and 5 grms. of manganese dioxide, in the way described by Mr. Stock, heating the mixture for ten minutes on a sand-bath. On distillation I obtained 0.15970 grm.  $\text{NH}_3$  or 100.7 per cent. of the quantity taken.

Another 20 c.c. of the solution were treated exactly the same as in the above experiment, except that the heating on the sand-bath was continued for three-quarters of an hour. I recovered 0.15844 grm.  $\text{NH}_3$  or 99.95 per cent.

The same quantity of the solution was then evaporated, and to it was added 1 grm. of pure cane sugar. It was now heated with 15 c.c. of strong sulphuric acid and 7 grms. of manganese dioxide. A dark green colour appeared after heating for fifteen minutes. The ammonia was distilled off, and gave 0.15923 grm.  $\text{NH}_3$ , or 100.4 per cent.

As the amount of ammonia taken was so small, I think that these results are quite passable.

A sample of Dog-biscuit was analysed by this method, and gave the following results:—

| <i>Kjeldahl.</i>         | <i>New Method.</i>       |
|--------------------------|--------------------------|
| 3.43 per cent. Nitrogen. | 3.51 per cent. Nitrogen. |
| 4.16 „ Ammonia.          | 4.26 „ Ammonia.          |

A sample of Cotton-meal gave good results:—

| <i>Kjeldahl.</i>         | <i>New Method.</i>       |
|--------------------------|--------------------------|
| 4.01 per cent. Nitrogen. | 3.94 per cent. Nitrogen. |
| 4.87 „ Ammonia.          | 4.78 „ Ammonia.          |



Wheat-flour is very easily analysed by this method, as it is in such a fine state of division. The results obtained were :—

| <i>Kjeldahl.</i>         | <i>New Method.</i>       |
|--------------------------|--------------------------|
| 1.73 per cent. Nitrogen. | 1.72 per cent. Nitrogen. |
| 2.10 „ Ammonia.          | 2.09 „ Ammonia.          |

Coffee is rather difficult to analyse, owing to an excessive amount of frothing when heated even gently with sulphuric acid and manganese dioxide, and also because some of the pieces of coffee are carried up the sides of the beaker by the froth, and remain unacted upon. This latter difficulty, of course, may be got over by reducing the coffee to a very fine powder. I find that the frothing is to a great extent avoided by heating the 2 grm. of the sample with 20 c.c. of concentrated sulphuric acid alone, and then, when the coffee is completely dissolved, cautiously adding the manganese dioxide. The mixture now simply requires to be left on the sand-bath until a green colour distinctly appears.

A sample of Coffee gave the following results :—

| <i>Kjeldahl.</i>         | <i>New Method.</i>       |
|--------------------------|--------------------------|
| 2.30 per cent. Nitrogen. | 2.23 per cent. Nitrogen. |
| 2.79 „ Ammonia.          | 2.70 „ Ammonia.          |

A sample of commercially pure Gelatin gave satisfactory results :—

| <i>Kjeldahl.</i>          | <i>New Method.</i>        |
|---------------------------|---------------------------|
| 15.68 per cent. Nitrogen. | 15.57 per cent. Nitrogen. |
| 19.04 „ Ammonia.          | 18.90 „ Ammonia.          |

I now proceeded to analyse six samples, rich in nitrogen, kindly given to me by Dr. Bernard Dyer, and in which he had estimated the nitrogen by the Kjeldahl method.

The following is a list of the substances examined, and the percentages of nitrogen (and ammonia) found in each, by Dr. Dyer and myself :—

#### LINSEED CAKE—

| <i>New Method.</i> |           | <i>Kjeldahl.</i> |           | <i>Dr. Dyer's figures (Kjeldahl.)</i> |           |
|--------------------|-----------|------------------|-----------|---------------------------------------|-----------|
| Nitrogen.          | Ammonia.  | Nitrogen.        | Ammonia.  | Nitrogen.                             | Ammonia.  |
| 3.49 p.c.          | 4.25 p.c. | 3.87 p.c.        | 4.70 p.c. | 3.91 p.c.                             | 4.74 p.c. |

#### CRUSHED HOOFS AND HORNS—

|            |            |            |            |            |            |
|------------|------------|------------|------------|------------|------------|
| 13.37 p.c. | 16.23 p.c. | 15.34 p.c. | 18.62 p.c. | 15.38 p.c. | 18.68 p.c. |
| 13.30 p.c. | 16.15 p.c. |            |            |            |            |

#### FISH GUANO (1)—

|           |           |           |            |           |            |
|-----------|-----------|-----------|------------|-----------|------------|
| 7.80 p.c. | 9.47 p.c. | 9.27 p.c. | 11.25 p.c. | 9.24 p.c. | 11.22 p.c. |
| 7.72 p.c. | 9.37 p.c. |           |            |           |            |

**FISH GUANO (2)—**

|           |           |           |           |           |           |
|-----------|-----------|-----------|-----------|-----------|-----------|
| 4.94 p.c. | 6.00 p.c. | 5.50 p.c. | 6.68 p.c. | 5.60 p.c. | 6.80 p.c. |
| 4.97 p.c. | 6.03 p.c. |           |           |           |           |

**DRIED BLOOD—**

|            |            |            |            |            |            |
|------------|------------|------------|------------|------------|------------|
| 10.81 p.c. | 13.12 p.c. | 12.93 p.c. | 15.65 p.c. | 13.08 p.c. | 15.88 p.c. |
| 10.82 p.c. | 13.14 p.c. |            |            |            |            |

**MANURE—**

|           |           |           |           |           |           |
|-----------|-----------|-----------|-----------|-----------|-----------|
| 5.56 p.c. | 6.75 p.c. | 6.16 p.c. | 7.49 p.c. | 6.09 p.c. | 7.40 p.c. |
|-----------|-----------|-----------|-----------|-----------|-----------|

Finally, a sample of pure ammonium sulphate was taken, which should contain, theoretically, 21.21 per cent. nitrogen, and on distilling the ammonia out of a known quantity I obtained 21.25 per cent. nitrogen. On treating another portion by the "Stock Method" I found 21.05 per cent. nitrogen. This shows that my standard solutions used in the analyses were practically correct.

On looking over the last six substances given above, one will observe that the higher the percentage of nitrogen the greater is the difference between the "Stock" figure and the Kjeldahl figure. However, the loss is not proportionate to the amount of nitrogen present, and, as will be seen from the following table, the percentage loss of nitrogen is by no means the same. Thus, in

The Linseed Cake the loss is 10.28 per cent of the total nitrogen present.

|                 |   |       |   |   |   |
|-----------------|---|-------|---|---|---|
| Hoofs and Horns | " | 13.15 | " | " | " |
| Fish Guano (1)  | " | 17.28 | " | " | " |
| " (2)           | " | 10.63 | " | " | " |
| Dried Blood     | " | 16.84 | " | " | " |
| Manure          | " | 9.30  | " | " | " |

The percentage of nitrogen found by the Kjeldahl process is taken as being the true percentage of nitrogen in the substances examined. There are several possible explanations of the deficiency, and I will enumerate a few of these.

(i.) The nitrogen in the presence of so much oxidizing agent may be oxidized to nitric acid straight away, and so be driven off.

(ii.) The ammonium sulphate formed may be further oxidized into nitrogen itself, or into some volatile compound of nitrogen.

(iii.) There may exist two different nitrogenous components in the above substances, one of which yields up its nitrogen, forming ammonium sulphate, while the other nitrogen is driven off by the strongly oxidizing mixture.

(iv.) The loss may result from some defect in the manipulation of the analyses, and this is, to some extent, borne out by the analyses I have given above. In the first experiments made it will be seen that the figures obtained

by both methods agreed fairly well with each other. It so happens that in these early analyses the manganese dioxide was added slowly, a little at a time, until I found out how much was required to quickly complete the oxidation and produce the green colour, which Mr. Stock says is an indication that the reaction is complete.

As soon as the requisite quantity was ascertained, it was added bodily to the substances, of which I afterwards give the figures. It is conceivable that in this case the large amount of oxygen present at one time was too much for the nitrogen, and that it is driven off, while in my former experiments the gradual addition of the manganese dioxide may only have produced sufficient oxygen to oxidize the sulphurous acid formed as the heating went on. When the substance was decomposed the green colour appeared, and no more dioxide was added. This part of the process requires further investigation, and I intend to do some more work on it.

I presume that a mixture of sulphuric acid and manganese dioxide acts on nitrogenous organic substances in much the same way as a mixture of sulphuric acid and potassium permanganate. It is known that the addition of potassium permanganate to a "Kjeldahl," even when all the organic matter is decomposed and the solution is colourless, may cause a considerable loss of ammonia.

In my experiments it always takes about ten minutes to a quarter of an hour to oxidize the substance. Mr. Stock says that he can carry out the operation in three to five minutes. Probably the difference in time required is due to the purity or impurity of the manganese dioxide used. Mine contains 40.86 per cent. of the dioxide. It is ordinary commercial powdered dioxide.

From the above experiments it is evident that the method requires a great deal more examination, and the cause of the loss of nitrogen discovering, together with, if possible, a preventative against the said loss, before the process can be used by analysts as a reliable one for the estimation of nitrogen in common organic substances.

#### DISCUSSION.

Mr. F. H. Perry Coste remarked, with regard to the results obtained by Mr. Skertchly, that in view of the very good correspondence between the figures in several instances, and also of the results on pure salts recently communicated by Mr. Stock himself, he did not attach much importance to the low nitrogen result with the ammonium sulphate; he had very little doubt that that was due to some oversight in working, and that Mr. Skertchly on repeating the experiments would obtain the full nitrogen.

The differences in the case of such samples as the *Hoofs and Horns* were, however, very important, for these might be taken as criteria; and any method that would yield the full nitrogen with such materials as these might safely be accepted as reliable for all ordinary work. Of course the differences were so great as to make it clear that the

Stock method was useless as a general analytical process at present ; but no one who had had personal experience in working out the Kjeldahl process would be hasty in finally condemning this new process on such grounds. It required long experimenting to bring the Kjeldahl process into thoroughly reliable working order, and he well remembered that for many weeks results were obtained regularly too low, very much as with the Stock method in the present case. As to the cause of the error here, having regard to the concordance between Mr. Skertchly's duplicates, he did not think it likely that the low nitrogen was due to any error in working ; the results seemed to him too constant for that. Two sources of error were possible. The whole of the nitrogen might be converted into ammonia, and then some of it oxidised into a nitrogen oxide by the continued action of the manganese oxide, just as he had found that a heavy loss of nitrogen might occur in the Kjeldahl process if, at the end of the digestion, permanganate were added and the digestion renewed. This was a *time reaction*, for instance, he (Mr. Coste) had proved in Dr. Dyer's laboratory several years ago that if pure ammonium sulphate sulphuric acid and mercury were boiled with potassium permanganate for increasing periods of time, increased losses of nitrogen took place. Now, if Mr. Skertchly would treat these samples by the Stock method for various times (say 5 to 10 or 15 minutes) then, if he found increasing losses of nitrogen, that would point to a similar danger. If, however, in such experiments the nitrogen remained constant though still too low, that would strongly point to the second possible cause of error being present, viz., that the nitrogen in such samples exists in at least two different forms, and that the Stock process fails to convert the whole. Considering the nature of these samples, that explanation had frequently suggested itself to Dr. Dyer and himself ; and this would account both for the agreement between Mr. Skertchly's duplicate "Stocks," though both so low, and also for the correct results obtained from other samples of a similar character. He hoped that Mr. Skertchly would continue these experiments, which were of great interest and value.

Dr. Bernard Dyer said that he himself had not yet found time to make any experiments with Mr. Stock's process. He was very anxious to get some personal experience of the process, and had been very pleased to give Mr. Skertchly those samples, so that by comparing results, he was enabled to get some indirect personal experience of what results the Stock process gave on materials of which he knew the composition.

The President wished to ask Mr. Skertchly whether he followed exactly the plan proposed by Mr. Stock, or in what way he altered it? Did he use the same quantities which Mr. Stock proposed, and did Mr. Stock lay down any rules as to the adding of manganese dioxide?

Mr. Coste assumed that in all these cases the distillations after the digestion in the Stock and Kjeldahl processes were carried out under equal conditions as to time and everything else.

Dr. Dyer, in reply to the question of a member, said that he had found no difficulty in obtaining acid which yielded practically no nitrogen. When a new bottle of acid was opened or a stock of caustic soda was made up, a complete blank experiment was made, going through the whole process, except that no nitrogenous substance was used, and the total allowance indicated for error and impurities from all sources came well within half a milligramme of nitrogen. There was no difficulty in getting sulphuric acid as pure as this.

Mr. Skertchly, in reply, said that as Mr. Stock had only used such small quantities, namely 0.5 to 1.0 gramme of the substances for analysis, he had thought it better to take somewhat larger amounts, up to 2 grammes. He first tried the process using the smaller quantity and the results thus obtained did not agree so well between themselves as when he used 2 grammes of the substance. Two grammes would give a better average sample than 0.5 gramme. With the larger amounts double the quantities of sulphuric acid and manganese dioxide were used. As to Mr. Coste's question, he would like to say that he gave one experiment with ammonium sulphate 10 minutes, and another three-quarters of an hour heating on the sand bath, and obtained the same results in both cases. With regard to the distillations, they were carried out under practically the same conditions.

He wished to thank Mr. Hehner for his kind assistance during the investigation.

The President said he was very glad to see that the Society had in Mr. Skertchly a new acquisition to those who read papers. It was highly desirable that young chemists, who became members, should attack matters requiring investigation, and give the Society the benefit of their experience.

Mr. Richmond read papers "On the action of some Enzymes on Milk-Sugar," and "The Estimation of Total Solids in Milk." With this the proceedings of the Society terminated.

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#### NEUTRALITY.\*

BY ALFRED H. ALLEN.

(Continued from page 192.)

I may say here that there appear to be good and bad kinds of methyl-orange in commerce, some giving very unsatisfactory results. I have elsewhere given the characters of a good article. In this connection I may mention that the colouring matter known as orange II. (helianthin being orange III.), or betanaphthol-orange, behaves in exactly the opposite manner to methyl-orange, becoming yellow in acid solutions and red in alkaline. Further, I have found it almost indifferent to ammonia. Unfortunately its reaction, even with caustic soda, is not sufficiently sharp to render it of practical value, or we should be in possession of a valuable indicator which would permit us to titrate caustic soda in presence of ammonia. Some valuable applications of such an indicator, if sufficiently delicate, at once suggest themselves.

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\* Abstract of a lecture delivered before the Chemists' Assistants' Association.

*Dimethyl-amido-azobenzene* itself, the colouring matter of which methyl-orange is the sodium sulphonate, has been recommended as an indicator by Fischer and Philipp, but R. T. Thomson considers it in no way superior to helianthin, the behaviour of which it in every way simulates. *Congo-red*, another indicator of the same class, is distinctly inferior to methyl-orange.

Mylius and Förster have suggested a method of titration in which iodeosin is employed. This colouring matter, though chemically related to phenolphthaleïn, as an indicator behaves like methyl-orange. That is to say, it is a tolerably strong acid itself and hence is not displaced from its compounds by very weak acids. Iodeosin presents no advantage when substituted for methyl-orange in ordinary titrations, but Mylius and Förster employ it in ethereal solution. Immediately there is the least excess of alkali the sodium salt is formed, and the colouring matter passes from the ethereal to the aqueous layer. With special care, and the use of water distilled in platinum, very minute traces of alkali can be determined in this way. (*cf.* THE ANALYST, xvi., p. 199.)

The explanation of the different behaviour of various indicators has received help from the thermo-chemical researches of Berthelot, who has pointed out that an acid which can be titrated accurately with methyl-orange is one the heat-formation of the solid potassium salt of which exceeds 10·2 calories. Phenolphthaleïn, on the other hand, enables us to titrate any acid the heat-formation of the potassium salt of which exceeds 6 to 7 calories. With Poirrier's soluble blue still feebler acids can be titrated, but the lower limit of its applicability has not been ascertained.

Mr. R. T. Thomson, of Glasgow, has investigated the behaviour of different indicators of neutrality in a remarkably complete and able manner, and his researches form in themselves a most valuable guide to the subject. I am indebted to Mr. Thomson's work for many of the facts respecting indicators mentioned in this paper. Mr. Thomson arranges the various indicators in three groups, to which Poirrier's soluble blue will form a fourth, thus :—

| Methyl-Orange Group.  | Litmus Group.                          | Phenolphthaleïn Group.      | Poirrier's Soluble Blue. |
|---|--|-----------------------------|--------------------------|
| Methyl-orange<br>Cochineal<br>Congo-red<br>Lacmoid<br>Iodeosin<br>Dimethyl-amido-azobenzene | Litmus<br>Rosolic acid<br>Phenacetolin | Phenolphthaleïn<br>Turmeric | Soluble Blue<br>CLB.     |

In the following table, which, with the exception of the last column, is due to Mr. R. T. Thomson (*Jour. Soc. Chem. Ind.* vi., 198), the figures represent the number of atoms of hydrogen displaced by sodium or potassium in the form of caustic alkali, when

a compound is formed having a neutral reaction to the indicator in question. Thus, when methyl-orange is used in the titration of sulphurous acid, the neutral point is reached when alkali has been added in quantity sufficient to form the compound  $\text{NaHSO}_3$ ; but when phenolphthaleïn is used the point of neutrality corresponds to the salt  $\text{Na}_2\text{SO}_3$ . By a combined use of the two indicators some valuable volumetric determinations can be affected.

| Acids.               |  | Methyl Orange.             | Phenolphthaleïn. |          | Litmus.         |          | Poirrier's Soluble Blue CLB. |
|----------------------|--|----------------------------|------------------|----------|-----------------|----------|------------------------------|
| Name.                | Formula.                                   | Cold.                      | Cold.            | Boiling. | Cold.           | Boiling. | Cold.                        |
| Sulphuric ... ..     | $\text{H}_2\text{SO}_4$                    | 2                          | 2                | 2        | 2               | 2        | 2                            |
| Hydrochloric ... ..  | $\text{HCl}$                               | 1                          | 1                | 1        | 1               | 1        | 1                            |
| Nitric ... ..        | $\text{HNO}_3$                             | 1                          | 1                | 1        | 1               | 1        | 1                            |
| Thiosulphuric ... .. | $\text{H}_2\text{S}_2\text{O}_3$           | 2                          | 2                | 2        | 2               | 2        | ?                            |
| Carbonic ... ..      | $\text{H}_2\text{CO}_3$                    | 0                          | { 1<br>dilute }  | 0        | —               | 0        | 2                            |
| Sulphurous ... ..    | $\text{H}_2\text{SO}_3$                    | 1                          | 2                | —        | —               | —        | 2                            |
| Sulphydric ... ..    | $\text{H}_2\text{S}$                       | 0                          | { 1<br>dilute }  | 0        | —               | 0        | ?                            |
| Phosphoric ... ..    | $\text{H}_3\text{PO}_4$                    | 1                          | 2                | —        | —               | —        | 3                            |
| Arsenic ... ..       | $\text{H}_3\text{AsO}_4$                   | 1                          | 2                | —        | —               | —        | 3                            |
| Arsenious ... ..     | $\text{H}_3\text{AsO}_3$                   | 0                          | —                | —        | 0               | 0        | 3                            |
| Nitrous ... ..       | $\text{HNO}_2$                             | { indicator<br>destroyed } | 1                | —        | 1               | 0        | ?                            |
| Silicic ... ..       | $\text{H}_4\text{SiO}_4$                   |                            | —                | —        | 0               | 0        | ?                            |
| Boric ... ..         | $\text{H}_3\text{BO}_3$                    | 0                          | —                | —        | —               | —        | 1                            |
| Chromic ... ..       | $\text{H}_2\text{CrO}_4$                   | 1                          | 2                | 2        | —               | —        | ?                            |
| Oxalic ... ..        | $\text{H}_2\text{C}_2\text{O}_4$           | —                          | 2                | 2        | 2               | 2        | 2                            |
| Acetic ... ..        | $\text{HC}_2\text{H}_3\text{O}_2$          | —                          | 1                | —        | { 1<br>nearly } | —        | 1                            |
| Butyric ... ..       | $\text{HC}_4\text{H}_7\text{O}_2$          | —                          | 1                | —        | { 1<br>nearly } | —        | 1                            |
| Succinic ... ..      | $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$ | —                          | 2                | —        | { 2<br>nearly } | —        | 1                            |
| Lactic ... ..        | $\text{HC}_3\text{H}_5\text{O}_3$          | —                          | 1                | —        | 1               | —        | 1                            |
| Tartaric ... ..      | $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ | —                          | 2                | —        | 2               | —        | 2                            |
| Citric ... ..        | $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ | —                          | 3                | —        | —               | —        | 3                            |

The behaviour of the alkaloids and organic bases with indicators has been very imperfectly studied. In the text-books it is frequently stated that such and such an alkaloid is distinctly alkaline (presumably to litmus), but it is only rarely and of recent years that chemists appear to have attempted to estimate alkaloids by titration with standard acid. Where this is desired, phenolphthaleïn is quite inapplicable, as already stated. Litmus answers in some cases, but by no means invariably, while with methyl-orange, in nearly all the cases hitherto tried, an accurate determination and a sharp end-reaction are obtainable.

In titrating an alkaloid with methyl-orange, it is rarely convenient to employ an aqueous solution of the base. A solution in proof spirit can be employed, but the indicator is much less sensitive under such conditions. I have found it preferable, especially when an alkaloid is much coloured, as is frequently the case in assaying bases directly extracted from their sources, to dissolve the alkaloid in a little ether, chloroform, amyl alcohol, or other suitable immiscible solvent. The solution is placed in a small stoppered cylinder, together with a few centimetres of water, coloured with a drop of methyl-orange solution. On then gradually dropping in the standard acid and agitating thoroughly after each addition, it is easy to observe the end of the reaction, as the colouring matter remains in the immiscible layer and presents a marked contrast to the red colour of the aqueous liquid. By using ether as a solvent for the alkaloid and titrating with  $\frac{N}{50}$  hydrochloric acid, I have obtained very satisfactory determinations of aconitine and its allies, even when working on as little as 0.030 gramme. This means the titration of the alkaloids from as little as three or four cunces of the tincture, or less than half-an-ounce of the aconite root.

In the following table I have compiled all the available information on the subject of the titration of alkaloids. The behaviour of numerous other alkaloids can be guessed at, but I have preferred to omit speculative statements. In the column headed 'methyl-orange,' accurate titrations can be made where the word *alkaline* is printed in italics. Where blanks are left the exact behaviour of the alkaloid is unknown.

It is evident that much remains to be done in this direction, and if some of the members of the Society will take the trouble to fill some of the gaps they will be doing a good work, and one which will be generally appreciated.

| Substance.     | Formula.   | Methyl Orange.  | Phenolphthalein. | Litmus.  |
|----------------|--|-----------------|------------------|----------|
| Methylamine    | $\text{CH}_5\text{N}$                            | <i>Alkaline</i> | —                | Alkaline |
| Trimethylamine | $\text{C}_3\text{H}_9\text{N}$                   | <i>Alkaline</i> | —                | Alkaline |
| Aniline        | $\text{C}_6\text{H}_7\text{N}$                   | Alkaline        | Neutral          | Neutral  |
| Pyridine       | $\text{C}_5\text{H}_5\text{N}$                   | <i>Alkaline</i> | Neutral          | Alkaline |
| Quinoline      | $\text{C}_9\text{H}_7\text{N}$                   | <i>Alkaline</i> | —                | —        |
| Antipyrine     | $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$   | <i>Alkaline</i> | Neutral          | Neutral  |
| Conine         | $\text{C}_8\text{H}_{17}\text{N}$                | <i>Alkaline</i> | Alkaline         | Alkaline |
| Nicotine       | $\text{C}_{10}\text{H}_{14}\text{N}_2$           | <i>Alkaline</i> | Alkaline         | Alkaline |
| Aconitine      | $\text{C}_{33}\text{H}_{45}\text{NO}_{12}$       | <i>Alkaline</i> | Neutral          | Alkaline |
| Atropine       | $\text{C}_{17}\text{H}_{23}\text{NO}_4$          | <i>Alkaline</i> | Alkaline         | Alkaline |
| Cocaine        | $\text{C}_{17}\text{H}_{21}\text{NO}_4$          | <i>Alkaline</i> | Neutral          | Alkaline |
| Morphine       | $\text{C}_{17}\text{H}_{19}\text{NO}_3$          | <i>Alkaline</i> | Faintly acid     | Alkaline |
| Codeine        | $\text{C}_{18}\text{H}_{21}\text{NO}_3$          | <i>Alkaline</i> | Alkaline         | Alkaline |
| Strychnine     | $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$ | <i>Alkaline</i> | Neutral          | Alkaline |
| Brucine        | $\text{C}_{23}\text{H}_{26}\text{N}_4\text{O}_4$ | <i>Alkaline</i> | Neutral          | Alkaline |
| Cinchona bases | —  | <i>Alkaline</i> | Neutral          | Alkaline |
| Caffeine       | $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$    | Alkaline        | Neutral          | Neutral  |
| Urea           | $\text{CH}_4\text{N}_2\text{O}$                  | Neutral         | Neutral          | Neutral  |



As an illustration of the application of the foregoing facts, we may take the case of a mixture of cinchona alkaloids. In the analysis of these the cinchonidine is usually precipitated from a neutral solution by means of Rochelle salt; the precipitate washed with cold water (thereby causing an uncertain loss), dried and weighed. Now, if, instead, the precipitate be washed once with a saturated solution of the precipitant (which has very little solvent action) and the filter containing the precipitate of cinchonidine tartrate and the adherent Rochelle salt be immersed in boiling water, the alkaloid can be determined in a few minutes by adding a drop of phenolphthaleïn solution and titrating with  $\frac{N}{20}$  caustic alkali. As Rochelle salt is perfectly neutral to phenolphthaleïn, and as tartrate of cinchonidine (or of quinine) acts just like an equivalent amount of free tartaric acid, the weight of alkaloid can be readily calculated from the measure of standard alkali used. Each 1 c.c. of  $\frac{N}{20}$  NaHO neutralised represents 0.0147 gramme of cinchonidine or (other alkaloid) precipitated as tartrate.

An exactly similar method is applicable to the treatment of the precipitate of quinidine hydriodide. This should be washed with a little neutral solution of potassium iodide instead of with water, and then immersed with the filter in boiling water. On titrating with  $\frac{N}{20}$  caustic alkali and phenolphthaleïn, each 1 c.c. of the standard solution represents 0.0162 gramme of quinidine precipitated as hydriodide. Of course this does not dispense with the necessity of making a correction for the amount of quinidine lost in the mother-liquor and washings.

**Hübl's Iodine-Absorption Method.** (*Helfenberger Annalen*, 1891, through *Chem. Zeit.* Compare THE ANALYST, xvii. 199.)—Investigations made in the chemical works of E. Dieterich, at Helfenberg, upon the Hübl method have led to the following conclusions :—

(1.) When the iodine solution is allowed to act for twenty-four hours or longer, and the absorption of the oil reckoned from comparison with a blank experiment made at the time of adding the iodine to the oil, the results obtained are too high, as the Hübl solution itself loses strength on keeping. The value obtained is higher the higher the temperature, the more recently the Hübl solution has been made up, the greater the excess of iodine, and the longer the time allowed for the completion of the reaction.

(2.) Results that are demonstrably too low, seeing that they may even be lower at twenty-four than at two hours, are obtained by taking the strength of the iodine solution as determined by a blank titrated at the end of the period of absorption, for the reason detailed in the foregoing abstract.

(3.) When a correction is made for the loss of strength of the excess only of the iodine solution as reckoned from the loss of strength of the blank titration during the period of absorption, the conditions recorded above as affecting results cease to exercise

any appreciably disturbing influence. (Contrast Holde's view—in preceding abstract—which is only tenable with the proviso that the large excess of iodine prescribed by him be used.)

(4.) Olive oil, tallow, oleic acid and lard give accurate iodine absorptions after two hours. Linseed oil, balsams, and resins, on the contrary, need longer exposure; (presumably, from the context—though it is not expressly stated—twenty-four hours).

Holde's contention that a large excess of iodine is necessary, is found by Dieterich to be true chiefly for drying oils. He considers that there should be an excess sufficient, in the case of drying oils, to use up 20-30 c.c. of decinormal thiosulphate, while an excess corresponding to 10-20 c.c. suffice for non-drying oils. The importance ascribed by Holde to the age of the Hübl solution is only legitimate as far as it implies that the solution should be rich in available iodine; otherwise more of it must be used.

The combined opinion of Fahrion, Holde (see preceding abstract), and Dieterich is that the solutions of mercuric chloride and iodine should be kept separate until one or two days before use, as the waste due to spontaneous weakening is less, but that solutions mixed *immediately* before use should not be employed, as the change in strength is greatest directly after mixing, and the alteration is too rapid to allow of accuracy.

B. B.

## REVIEW.

THE PRINCIPAL STARCHES USED AS FOOD. W. GRIFFITHS. (Baily & Son, Cirencester, Price 5/-.)

This handy little book contains a short and concise description of some twenty-four varieties of the principal starches usually met with, each being illustrated by a photo-micrograph. Though excellent illustrations of these objects are to be found in works on Botany, Food Analysis, &c., in the form of copper-plate engravings, lithographs or wood cuts, this is the first time, to our knowledge, that they have been portrayed by photography and collected in book-form. The best method of identifying an unknown starch is the somewhat tedious one of comparing it with actual samples of other starches under the microscope; the next best is undoubtedly to use for comparison a series of well-executed photographic representations of such samples. This latter function the book fulfils admirably; the illustrations are beautifully clear and distinct, the characteristics of each individual starch being prominently brought out. Specially interesting is the photograph of the not-generally-known starch from the fruit of the potato, which the author characterises as "the most beautiful of all starches." It somewhat resembles that of the tuber, but is much larger.

The book cannot fail to be of value to analysts, who are so frequently called upon to identify starches used for the purpose of adulteration.

# THE ANALYST.

DECEMBER, 1892.

## TO OUR READERS.

IN consequence of the great pressure on the space hitherto available in *THE ANALYST*, and of the impossibility which has existed of reproducing many articles of interest and utility to Analysts, it has been decided to permanently enlarge the Journal with the commencement of the new volume in January next. From that date the price to annual subscribers, in advance, will be 10s. 6d. per annum, post free; the price for single numbers being one shilling. As there are very few back volumes of *THE ANALYST* in existence, the price of these will be from this date one guinea each.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A Meeting was held at the Rooms of the Society of Arts, John Street, Adelphi, on Wednesday, the 2nd of November, the chair being occupied by the President (Mr. O. Hehner).

The minutes of the last meeting were read and confirmed, and papers read on the following subjects:—"Note on a sample of poor, but undoubtedly genuine, Milk," by Mr. C. W. Heaton; "An abnormal sample of Milk," by Dr. Bernard Dyer; "Composition of an abnormal sample of Milk," by Mr. Alfred Smetham; "Some abnormal Milks," by Mr. H. Droop Richmond; "An abnormal sample of Milk," by Mr. W. Foulkes Lowe.

The reading of these papers was followed by a long and animated discussion.

MR. H. D. Richmond then exhibited and explained the working of

### AMAGAT AND JEAN'S OLEOREFRACTOMETER.\*

Dr. Muter having been asked (as the original introducer of the instrument to British Analysts) to give his experience of its working, said:—

He had no doubt of the general utility of the instrument, and he considered it a profitable investment on the part of any public analyst in considerable practice. Like

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\* For full description and illustration, see *THE ANALYST*, vol. xv., page 87,

every other special appliance, it had its advantages and its drawbacks. Its use depended to a considerable extent on "personal equation," and on the exercise of care in the selection and preservation of the typical oil employed. Analysts using it should make their own standard observations, and not go blindly upon the published figures of other observers. So long as the instrument was only used for oils, the typical oil once placed in the outer casing of the prism would keep good for a long time, but when solid fats (such as butter) were worked with, the continued heating and cooling of the oil caused it to become cloudy, owing to the crystallization of the stearin, and then wrong results were obtained. Under such circumstances it was necessary to change the oil more frequently, and to make a test of the zero with fresh typical oil in the inner prism each day before commencing work. In dealing with butter it was undoubtedly better to heat the sample 20 degrees above the required temperature, place it in the prism, allow it to gradually cool down, and then to read the moment that the two thermometers marked the same degree. The vital point was that the oils inside and outside the prism must both be exactly at the same temperature. It was a very useful instrument for sorting butters, and so long as the present limit of "Reichert" continued to be a force, it would be found of no use to go on with any ordinary butter showing between 28 and 34 on the oleorefractometer. If over 34 or under 28 "Reichert" would be necessary, in the former case to prove a possible addition of cocoa-nut fat, and the latter for small percentages of ordinary fat. If the refraction was 20, or under, then the article must be at least a half-and-half margarine, and no "Reichert" was necessary to follow to confirm, as the sample could be definitely charged with being what is legally called margarine, and not butter. The practical use of the instrument was, therefore, to rapidly detect all cases of undoubted margarine, and also of definitely pure butter, but for any doubtful cases "Reichert" must follow and be considered side by side with the refraction.

This terminated the proceedings of the Society.

## THE ACTION OF SOME ENZYMES ON MILK-SUGAR.

BY H. DROOP RICHMOND.

*(Read at the Meeting on October 5th, 1892.)*

THESE short notes formed part of an investigation of the methods for the complete analysis of milk and milk products. They were originally intended to see if rennet had any action on milk-sugar; it seemed very unlikely that this was the case, but being unable to find any experiments actually proving this, I decided to try for myself. I was also led to investigate this on account of Pappel and myself having isolated from gamoose milk a sugar, towf'ose (tewfikose) by a method which avoided the use of rennet, and it appeared just possible that milk sugar might be formed from some compound existing in the milk by the action of rennet.

I assume that all sugars having the same rotary and reducing powers as milk-sugar are that compound, and that if the rotary and reducing powers do not alter, that the milk-sugar is unchanged. This assumption, I take it, will be granted by all.

The polariscope used was the Mitscherlich half-shadow polariscope described by Vieth (ANALYST, xi. 141); it is not a very delicate instrument, but I find that I can read to  $\cdot 025^\circ$ , by taking the average of several (say 10) readings. In the paper referred to Vieth states that the readings may be taken as giving grams of milk-sugar in 100 c.c. This, I find, is not quite, though nearly accurate. The tube used has a length of 198.2 millimetres, and the scale is divided into angular degrees; taking the specific rotary power  $[\alpha]_D$  of milk-sugar to be  $52.5^\circ$  (c.f. Wiley, *Amer. Chem. J.*, vi. No. 5) the readings would require to be divided by 1.042 ( $\frac{100 \times 100}{198.2 \times 52.5} = \frac{1}{1.042}$ ). I have made many experiments to determine the actual factor, and find that the readings require to be divided by 1.045 to give grams per 100 c.c. These two factors agree well within the limit of reading.

I find, on the examination of the published statements as to the reducing power of milk-sugar, that some diversity of opinion occurs as to the method of obtaining accurate results. Thus, Soxhlet (*J. f. Prakt. Chem.* [2] xxi. 277, *et seq.*) finds that the same results are obtained whether the Fehling's solution be diluted or not; the conclusion of Rodewald and Tollens (*Ber.*, xi. 2076) does not quite accord with Soxhlet's. Muter (ANALYST, v. 35) indicates that, in order to ensure constant results, the sugar must be diluted till the solution contain less than .1 gram in 100 c.c., and a very slight excess of Fehling's solution must be added. Jones (ANALYST, xiv. 81) employs O'Sullivan's method, in which a large excess of Fehling's solution, diluted with two measures of water, are employed, and brought to the temperature of the water-bath before the sugar is added, and the heating is continued for 14 minutes.

I have made some experiments on this subject, and find that O'Sullivan's method gives the most concordant results. I also find that, if the Fehling's solution is diluted with an equal bulk of water, I obtain the same results as when diluting with two volumes of water, and there is less solution to be filtered. I collect the precipitate of  $\text{Cu}_2\text{O}$  on a filter, and burn first over a bunsen and then in a muffle. Duplicates do not differ more than about 1 milligram. I find that the filter absorbs 2 milligrams from the Fehling's solution, and therefore deduct this. Jones gives the factor to convert copper oxide into milk-sugar (anhydrous) as 0.6024. I myself find 0.6025, and calculate from the mean of Rodewald and Tollens' results the factor 0.6022.

The method and factor given in the valuable paper of Jones are therefore to be relied upon.

My first experiments were made by taking milk and estimating therein the milk-sugar, and estimating the milk-sugar in the whey produced by rennet in the same milk, and calculating the proportion of the milk-sugar to 100 parts of water in each.

The mean of three experiments gave—

|                        | Milk. | Whey. |
|------------------------|-------|-------|
| Milk-sugar (polarised) | 5.30  | 5.31  |
| „ (gravimetric)        | 5.28  | 5.28  |

Rennet has therefore no action on milk-sugar, and milk-sugar exists in the milk as the same compound which exists in the whey.

I next made a solution of milk-sugar; 25 grams of finely-powdered milk-sugar, which had been very carefully purified by Dr. Vieth, were shaken for five minutes with 450 c.c. of cold water, and immediately filtered, and the solution mixed and polarized. The readings were taken at from 7 to 8 minutes after the addition of the sugar to the water; after a further ten minutes, the readings were again taken; and again at intervals of quarter-hour, half-hour, one hour, six hours, and twenty-four hours. Taking the first reading to have been at an interval of five minutes from the mean time of solution, I constructed a time-curve for the fall in rotary power, and from this calculate that at the moment of solution the specific rotary power is  $82.0 \pm .2$ . I also estimated the density of the solution at  $15.5^{\circ}$  after an interval of ten minutes, and after an interval of twenty-four hours. In each case it was 1.0193, showing that no change in the density had occurred concurrently with the change in the specific rotary power.

This solution contained 5.20 grams in 100 c.c. of milk-sugar determined by evaporation, 5.22 grams by the polariscope, and 5.18 grams from the weight of the copper oxide reduced, and 5.17 grams from density.

With this solution the following experiments were tried:—

*Action of rennet.*—To 50 c.c. of this solution 10 milligrams of rennet were added, and this was kept at  $40^{\circ}$  C for one hour. After cooling and filtering, it gave the following:—

|                   |      |
|-------------------|------|
| Sugar (polarised) | 5.22 |
| „ (gravimetric)   | 5.23 |

This shows again that rennet has no action on milk-sugar.

*Action of pepsin.*—To 50 c.c. of this solution 5 c.c. 1% hydrochloric acid and .03 grams of pepsin were added, and the solution heated for 3 hours at  $40^{\circ}$  C. After cooling, filtering, and correction for the small figures obtained in a blank experiment, the following figures were obtained:—

|                   |      |
|-------------------|------|
| Sugar (polarised) | 5.24 |
| „ (gravimetric)   | 5.19 |

Pepsin is without action on milk-sugar.

*Action of pancreatic extract.*—To 50 c.c. of this solution were added 1 c.c. of pancreatic extract, and .05 grams of sodium bicarbonate, and the whole digested at  $55^{\circ}$  C for

one hour. After cooling, filtering, and correction for the small figures obtained in a blank experiment, the following figures were obtained:—

|                   |      |
|-------------------|------|
| Sugar (polarised) | 5.22 |
| „ (gravimetric)   | 5.17 |

Pancreatic extract has then no action on milk-sugar.

In the experiments quoted in no case was the enzyme destroyed by heating before estimating the sugar. It was found, in all cases, that while the reducing power was only slightly affected thus, the specific rotary power was diminished (in the case of pepsin digestions the acid being first neutralized). Experiments on milk showed also that the specific rotary power of the sugar is reduced by heating. The study of the changes of milk-sugar by heat is reserved for a future communication.

These experiments show that the milk-sugar in whey and in artificially digested milk can be accurately estimated, provided that they have not been heated.

The change of rotary power on heating milk-sugar (in solution) shows that some chemical change is taking place. This sheds some light on the fact that constant results cannot be obtained on continued drying of the total solids of milk unless the water is rapidly evaporated. I have noticed that if precautions are taken to get rid of the bulk of the water in a short time (*c.f.* ANALYST, xiv. 121) that the residue does not turn brown on continued heating. As in ordinary total solid estimation about one hour elapses before the residue is apparently dry, there is sufficient time allowed for considerable decomposition, which may (and probably does) render the results inaccurate. On this point I believe that my investigation of the changes of milk-sugar on heating will shed considerable light.

[NOTE.—With reference to the slight error involved by taking the reading of the Mitscherlich half-shadow polariscope to indicate grams of milk-sugar per 100 c.c., Dr. Vieth writes me that he has long been aware that it is not correct; but as the error introduced is small, he has preferred to call the actual readings milk-sugar on account of practical convenience. The mean of Dr. Vieth's readings on accurately prepared solutions of milk-sugar gives the factor 1.044.—H. D. R.]

## THE ESTIMATION OF TOTAL SOLIDS IN MILK.

PRELIMINARY NOTE BY H. DROOP RICHMOND.

(*Read at the Meeting on October 5th, 1892.*)

THE proportion of total solids in milk is always estimated by evaporating the water, and weighing the residue; the most usual method is that adopted by the Society of Public Analysts, to evaporate 5 grams of milk in a basin to practical constancy.

A very superficial observer cannot but be struck by the fact that the residues are always more or less brown in colour, and the sole inference that can be drawn from this

fact is that some decomposition takes place. This was realized by Wanklyn more than 20 years ago, and to avoid this he recommended that the limit of drying should be three hours, in which time he assumed the water to be completely driven off, and no decomposition to have commenced; he assumed that by three hours drying the milk-sugar was not dehydrated. The results of Erdmann, Schmoeger, and Urech render this last assumption unlikely. It is evident from the application of simple physical laws that constant results cannot be obtained thus, unless either a large margin of time be allowed, or unless various conditions, such as the hygrometric state of the air and the rate of evaporation, can be kept constant; neither of these conditions obtain in practice, and therefore Wanklyn's method cannot be included among those to which consideration need be given.

Among other methods for the estimation of total solid may be mentioned those of Gerber and Radenhansen who curdle the milk previously to evaporation by the addition of either acetic acid or alcohol; they give the preference to alcohol on account of its greater rapidity and accuracy; within late years the use of acetic acid was resuscitated, and I believe claimed as original, by Johnstone.

Duclaux considers that sponge is the best medium on which to dry the residue; he employs a U-tube of peculiar shape immersed in boiling water, through which a current of air is aspirated. Gannter uses wood pulp in a basin. Adams' paper method is too well known to need any description. Babcock and Macfarlane have each described substantially the same method of drying the residue on asbestos contained in a glass tube. Muter and others dry on sand, and Muter has also used copper oxide for the purpose.

Storch uses pumice as a medium for evaporating milk.

I have proposed drying about 1 gram in a wide platinum basin, spreading well over the bottom during the evaporation.

It is noticed that if the milk is greatly spread out and the evaporation proceeds very quickly, that the residue remains white, showing that the same decomposition is not taking place.

I find that none of these methods are free from objection; Gerber and Radenhansen's methods do not give a white residue, and the residues lose weight almost indefinitely on drying continually. The same applies to the S. P. A. method, and for this reason it is directed to dry to practical constancy. It is at once evident that one experimenter's idea of practical constancy may not be the same as another's, and results may and do differ somewhat. The methods of Duclaux, Gannter, and Adams necessitate the previous drying of somewhat hygroscopic substances. The methods of Babcock, Macfarlane, and Muter involve the use of apparatus which is not so convenient as a basin, while in my own method so small a quantity must be used that errors of weighing



are greatly multiplied. The use of sand and pumice I find does not sufficiently effect the spreading of the milk over a large surface.

For these reasons I have tried the use of asbestos contained in a platinum dish; I place about 3 grams of asbestos (of the best quality) in a platinum basin, and ignite;\* I weigh this, add 5 grams of milk, and dry on the water bath for about two hours, and then leave it in the air or water-oven at about 98° for twelve hours or more (usually over night); I find that I can obtain absolutely constant weight, a further drying for 24 hours, even at 105°, does not affect the weight as much as a milligram, and as some of the weighings are less and some more, I attribute any minute difference to errors of weighing; the residue serves excellently for the purpose of ash estimation.

I find that this method agrees very well in duplicate, and with my former method, and is about 0.1 per cent. higher than my own S. P. A. method determinations; I have used it on samples which were analysed in duplicate by two other chemists by the S. P. A. method, and it agrees almost exactly with the results of one, but is slightly lower than those of the other; my S. P. A. results are the lowest of the three, indicating that in the S. P. A. method there is a personal error to be considered. I do not wish to attack the S. P. A. method, as the differences are small and rarely exceed  $\frac{1}{4}$  per cent., which is in practice a very good agreement, but am endeavouring to find a method which can be relied upon for scientific purposes; I do not yet claim that the method described above is accurate, as I am fully aware that agreement of duplicates, prevention of browning of the residue, and constant results do not prove accuracy, though the contrary holds. I am working to obtain proof that this method is accurate, and have brought this forward as a preliminary notice, in order that my fellow experimenters may also test it, and I shall be happy to exchange samples with any chemist who may communicate with me, with a view to test it, and to see if there is a personal error.

## ON THE BABCOCK METHOD OF MILK ANALYSIS.

BY FRANK T. SHUTT.

In a paper recently read before the Society of Public Analysts on the Determination of Fat in Milk, Mr. Stokes quotes *some* of my results obtained by the Babcock method, neglecting others, and entirely ignores my conclusions. My paper on this question has already appeared *in extenso* (*Chem. News*, lxiv., 4), so I could not expect you to publish it. I would, however, request space to place before your readers such extracts from it as will make clear my reason for believing this to be a most admirable dairy process.

### *Examination as to Reliability and Accuracy.*

Thirty-two samples of milk have been examined in duplicate by (1) the Babcock test and (2) by gravimetric analysis, the results by the latter being taken, for the sake of comparison, as correct. These operations gave us 128 independent fat determinations.

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\* To ignite asbestos to constant weight, it is necessary to use a muffle, since by ignition over a bunsen or blowpipe the total combined water is not always lost.

As the results obtained throughout the whole series are uniformly close, it will suffice here to tabulate a few of them as examples :—

| No. | Percentage of Fat by Babcock method. | Percentage of Fat by gravimetric analysis. |
|-----|--------------------------------------|--|
| 1   | { 4.4<br>4.4                         | 4.54<br>4.56                               |
| 2   | { 3.4<br>3.5                         | 3.58<br>3.56                               |
| 3   | { 3.6<br>3.5                         | 3.72<br>3.76                               |
| 4   | { 4.8<br>4.8                         | 4.90<br>4.91                               |
| 5   | { 5.8<br>5.9                         | 6.04<br>6.07                               |
| 6   | { 3.5<br>3.3                         | 3.40<br>3.35                               |
| 7   | { 3.4<br>3.5                         | 3.60<br>3.62                               |
| 8   | { 3.8<br>3.7                         | 3.68<br>3.68                               |
| 9   | { 3.8<br>3.9                         | 3.87<br>3.88                               |
| 10  | { 4.0<br>4.0                         | 4.04<br>4.03                               |
| 11  | { 3.3<br>3.3                         | 3.32<br>3.33                               |
| 12  | { 3.5<br>3.7                         | 3.70<br>3.69                               |

An inspection of this table will reveal (1) the limits within which the amount of fat will vary when the Babcock test is made in duplicate, and (2) the approximation of such results to those given by carefully conducted chemical analyses.

Of the thirty-two samples tested in duplicate by the Babcock method, only two gave a difference between their duplicates amounting to three-tenths (.3) of one per cent. ; two varied in their duplicates two-tenths (.2) of one per cent. ; fourteen differed to the extent of one-tenth (.1) of one per cent., and thirteen gave results identically the same.

The greatest difference between fat determinations by the Babcock test and gravimetric analysis on the same milk was (.25) a quarter of one per cent. This occurs in three instances only. Where the results are not identical, the variation is usually between one-tenth and two-tenths of one per cent.

From these data therefore we may safely conclude that when the Babcock test is made according to the instruction given with the machine, *strictly reliable results are*

obtained, and that the percentage of fat so found, allowing for the greatest error possible under such circumstances, will be well within one-quarter of one per cent. ( $\cdot 25$ ) of the amount of fat actually contained in the milk.

Since the publication of the above, I have made many trials towards applying the method to the testing of composite samples, and have met with gratifying results, as the following record, taken from many others of a like degree of accuracy, will show. In addition to the usual Babcock apparatus, a special pipette delivering 2.92 c.c. is all that is necessary—no preservative, poisonous or otherwise, being requisite to the accurate working of the test. To obtain the average percentage of fat in a cow's milk, or of milk supplied by the vendor, for a period extending over six days, successive measures of milk should be delivered from this pipette daily into an ordinary Babcock bottle. This composite sample is then treated with sulphuric acid in the usual manner. The percentage of fat so found is equivalent to the mathematical average of daily trials. The curdling of the milk in the bottles before the expiration of the period—which always occurs—apparently in no way vitiates the accuracy of the result.

| Day.   |     |     |     |      | Quantity. |     |  | Percentage of Fat. |
|--|-----|-----|-----|------|-----------|-----|--|--------------------|
| Monday                                       | ... | ... | ... | {    | 17.6 c.c. |     |  | 3.5                |
|  |     |     |     |      | 17.6      |     |  | 3.6                |
| Tuesday                                      | ... | ... | ... | {    | 17.6      |     |  | 3.3                |
|  |     |     |     |      | 17.6      |     |  | 3.2                |
| Wednesday                                    | ... | ... | ... | {    | 17.6      |     |  | 5.4                |
|  |     |     |     |      | 17.6      |     |  | 5.4                |
| Thursday                                     | ... | ... | ... | {    | 17.6      |     |  | 4.7                |
|  |     |     |     |      | 17.6      |     |  | 4.7                |
| Friday                                       | ... | ... | ... | {    | 17.6      |     |  | 3.4                |
|  |     |     |     |      | 17.6      |     |  | 3.4                |
| Saturday                                     | ... | ... | ... | {    | 17.6      |     |  | 4.6                |
|  |     |     |     |      | 17.6      |     |  | 4.6                |
| <hr/>  |     |     |     |      |           |     |  |                    |
| Average of above                             |     |     | ... | ...  | ...       | ... |  | 4.15               |
| Monday to Saturday<br>inclusive, composite } |     |     | {   | 2.92 |           |     |  | 4.2                |
|  |     |     |     | 2.92 |           |     |  | 4.2                |

It is scarcely necessary to remark that this modification effects a great saving of time, while I think it is safe to infer from the above results that it entails no loss of accuracy.

The Babcock method, using composite samples, offers a cheap and reliable means of estimating fat in milk, and undoubtedly in the near future it will be widely used in all places where milk is valued and paid for according to its fat contents.

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**The use of Centrifugal Machines in Analytical and Microscopical Work.** W. Thorner. (*Chem. Zeit.*, 1892, xvi., 1101-1104.)—The author has, on former occasions, shown the utility of a centrifugal apparatus for facilitating analytical and microscopical work (*ANALYST*, 1891, p. 210), and has now collected his experiences in a single article, to which additions based on subsequent experiments have been made. The instrument he uses is the Victoria Separator, by Watson, Laidlaw & Co., of Glasgow. A modification of the instrument has been introduced, consisting in an iron case with a removable cover surrounding the centrifugal plate, bearing the tubes containing the substances under treatment, which is designed to prevent accident should breakage occur. No such accident has happened in the author's experience; but the case is useful as lessening the resistance to rotation on account of the air inside the box being rotated with the tubes, and therefore stationary relative to them. The centrifugal plate, which is a stout, well-tinned brass casting, is made in two sizes, 160 and 240 mm. in diameter, and is fitted with metal tubes or cases, with an internal diameter of 19 and 36 mm., for the reception of the glass tubes in which the operations are conducted. The larger plate is arranged to take 8 small cases, 16 mm. in diameter, for fat determinations in milk, while the smaller plate is provided with two of the larger and two of the smaller cases, so as to adapt it for more general purposes. Special larger cases can also be used, with a capacity of as much as 400 c.c.; but when using vessels of this size, care must be taken to balance the machine with another cylinder of similar weight, a precaution of general applicability. The cylindrical metal cases for the reception of the glass tubes are made of well-tinned sheet brass or copper, and are provided with a cotton pad, to avoid risk of breaking the tubes dropped into them. Tubes, of which the lower part is narrowed and graduated, are supported in a wooden block, similarly shaped, and slipped into the metal case.

The use of these various apparatus is shown by the following examples:—

(1.) *Determination of fat in milk and milk products.*—10 c.c. of the well-mixed sample are placed in a tube with a narrow graduated neck, 1.5 c.c. of alcoholic potash containing 160 grammes of KOH per litre, or 1 c.c. of an aqueous solution of 500 grammes KOH per litre, added and mixed therewith by gentle shaking. The tube has a wide collar above the narrow neck, and it is hung by means of this in a boiling water-bath, the screw-clip on the rubber tube carried by the cork in its mouth, being closed after 10-15 seconds, when the alcoholic liquid (if that has been used) begins to boil. The tube is removed from the bath after 2-3 minutes, again shaken gently, and glacial acetic acid run in by means of a tap funnel until the liquid is above the zero mark on the narrow neck. Further shaking, and the addition of more acid may be necessary to complete the solution of the casein. The rubber cork is then replaced, and the tube again hung in the water-bath, from which it is removed after some minutes, the screw-clip opened, the cork taken out, and the tube rotated in the separator at 2,000 or 3,000 revolutions per minute,

according as the larger or smaller plate is being used. The tube is then returned to the bath, and brought to a temperature of  $100^{\circ}\text{C}$ . before reading off the fatty acids. The results agree with those obtained by gravimetric methods. Eight determinations of fat can be made in twenty minutes.

(2.) *Determination of cream.*—This can be done by 10-15 minutes' rotation of 20 c.c. of milk. The end is more easily attained by diluting the sample with an equal volume of water, and doubling the observed reading.

(3.) *Determination of the contents of water in butter and other fats.*—The lower part of the centrifugal tube is contracted and graduated. 10 c.c. of the fat are used, and the results up to a content of 30 per cent. by volume are exact to 0.2 per cent. The butter is measured by the little apparatus described in a previous abstract. (THE ANALYST, 1891, p. 210.)

(4.) *Determination of fat (or more strictly fatty acids) in butter and other fats.*—A tube with a narrow graduated neck, like that used for milk, but without the stopper and screw-clip, is used. The same apparatus serves for the determination of fatty acids in soap, and the content of mineral oil in mixed lubricants.

(5.) *Testing flour and meal.*—The apparatus for the separation of various flours and meals has already been described (THE ANALYST, p. 210, 1891). The microscopic examination of meals and starches is facilitated as follows: 5-10 gms. of the meal are stirred with a little cold water, poured into 500 c.c. of hot water, and heated for half hour on the water-bath. About 100 c.c. of the well-mixed contents of the flask are treated with 1 c.c. of 50 per cent. KOH solution, and another similar quantity with 5 c.c. of glacial acetic acid, and again heated on the water-bath. The liquid is then rotated in a plain cylindrical tube for five minutes, and the resulting residue at the bottom of the tube examined microscopically.

(6.) *Examination of tuberculous sputum.*—The sputum is mixed in a plain cylindrical tube, after the addition of at least an equal volume of hot water or dilute solution of borax, well shaken, heated in the water bath for ten minutes and rotated briskly for 5-10 minutes. The residue at the bottom of the tube is then examined according to known methods. Very viscous samples are best treated by the addition of a few drops of 50 per cent. KOH solution before heating and rotating. The residue can be washed, if thought necessary, by subsequent rotating with water.

(7.) *Examination of milk for tubercular bacilli.*—20 c.c. of the sample are mixed with 1 c.c. of 50 per cent. KOH and rotated in a plain cylindrical tube, heated for two minutes, 20 c.c. of glacial acetic acid added, the whole well mixed, heated again for three minutes until the casein is dissolved, and rotated for ten minutes at 3,000 revolutions per minute. The residue is washed by rotation with 40 c.c. of hot water for ten minutes, and then examined microscopically, as usual.

(8.) *Examination of urine.*—50 c.c. of the sample are placed in a tube with the lower part contracted and finely divided, so that its total capacity is 0.5 c.c. and 0.005 c.c. can be read, and rotated briskly for five minutes. Should the urine be only slightly turbid a larger quantity, *e.g.*, 100 to 400 c.c., must be used in a larger tube, the residue from which is then treated in the smaller tube with the fine divisions. The residue is examined microscopically. The author has succeeded in detecting tubercular bacilli in urine, with and without staining. The method would probably be available for the determination of albumen, but experiments on this point are not yet complete.

(9.) *Determination and examination of turbidities in wine, beer, etc.*—The methods used for urine are applicable here.

(10.) *Examination of water.*—100 c.c. of the water to be examined are rotated for ten minutes in order to induce the ready settlement of any bacilli, etc., that may be present; a little fine sterilised elutriated clay or talc is added, about 0.1 c.c. being shaken up with the water before rotation. Waters naturally slightly turbid with clay or ferric hydrate, of course, need no such addition. The residue is washed by rotating it in a narrow tube, the bottom of which is contracted like that used for urine, with 30–50 c.c. of water for ten minutes. The finest residue is used for the preparation of plate cultivations on alkaline or slightly acid gelatin in the usual way.

(11.) *Volumetric determination of precipitates in analysis.*—When the quantity of liquid is small, *e.g.*, under 50 c.c., the precipitation can be conducted in the tube with the contracted lower part, already mentioned, and the volume of the precipitate read off after rotation. In the case of larger quantities a larger tube is first used in which the ordinary operations usually carried out in a beaker or flask, including even heating (with caution) over a naked flame, are performed, and the precipitate transferred after rotation to the smaller tube, and treated as before. In order to obtain accurate results a standard time and rate of rotation must be adopted.

The apparatus described above can be obtained from Dierks & Möllmann, of Osnabrück. B. B.

**Influence of the Sulphur in Coal Gas on Determinations of Sulphur by Fusion.** Van Leeuwen. (*Rec. Trav. Chim. Pays-Bas*, 1892, xi. 103, through *Chem. Zeit.*)—The author's experiments were carried out on spent gas-works purifier, of which 0.5–0.6 was treated with 35 grms. (!) of a mixture of 1 part of potassium chlorate and 6 parts of sodium carbonate, in a platinum dish either covered with a porcelain lid, or with another inverted platinum dish, for  $2\frac{1}{2}$  hours over a bunsen burner. The percentages of sulphur found in three determinations were 49.34 per cent., 48.55 per cent., 47.98 per cent., giving a mean of 48.63 per cent. Two blank experiments showed that a quantity of sulphur was absorbed from the gas amounting to 2.4 per cent. and 3.3 per cent. reckoned on a 0.5 gm. of the substance in which sulphur was to be determined.

As the coal gas used did not blacken lead paper, it appeared that the sulphur was present as carbon disulphide, or some analogous compound, and the author repeated the experiment, using in one case the unpurified gas, and in the other gas that had been passed over pumice saturated with an alcoholic solution of caustic potash. The first gave an amount of sulphur corresponding to 4 per cent. of sulphur reckoned on 0.5 grm. of the substance to be analysed, while the second only yielded a quantity equivalent to 0.1 per cent. Three determinations of sulphur in the spent purifier, of which the figures obtained with ordinary coal gas are given above, gave 46.97 per cent., 46.26 per cent., and 46.29 per cent., that is a mean value of 46.50 per cent., against the former result of 48.63 per cent. The author recommends for such purposes as those described the new Barthel's burner, fed with benzine free from sulphur, or with alcohol.

B. B.

[NOTE BY ABTRACTOR.—The errors here detailed are real and serious, but they can be most readily and certainly avoided by the use of the gas muffle.]

**The Gravimetric Determination of Sulphur.** M. Ripper. (*Zeits. anorg. Chem.*, 1892, ii. 36, through *Chem. Zeit.*)—The reduction of barium sulphate to sulphide, which the author considers to take place when the former substance is incinerated according to the modern method of placing the precipitate in a crucible together with the filter paper, both in a moist state, and slowly drying and burning, can be conveniently remedied by the addition of a few drops of bromine water, until it ceases to be decolorised, before the purification of the barium sulphate with hydrochloric acid. This treatment with bromine water is, of course, repeated after the barium sulphate has been purified with hydrochloric acid and again incinerated.

B. B.

**A New Process for the Separation of Iron.** J. W. Rothe. (*Mitt. könig. tech. Versuchsanstalten*, 1892. x. 132, through *Chem. Zeit.*)—The process depends on the observation that ferric salts in hydrochloric solution of suitable concentration, yield the whole of their iron as ferric chloride when shaken out with ether. Ferrous salts are not dissolved out by ether under like conditions. Manganous salts, chromic salts, and those of nickel and aluminium, give no soluble compounds when thus treated. Cobaltous and cupric salts are soluble to nearly the same extent in ether, the exact amount varying with the quantity present, but it is in any case very small. What is extracted can be got rid of by shaking out the ethereal solution of ferric chloride with hydrochloric acid of specific gravity 1.04, and the small quantity of iron thus extracted can be recovered by renewed treatment with ether.

In the case of iron and steel, the method is worked as follows:—Five grms. of the sample are dissolved in hydrochloric acid of specific gravity 1.124 at 19°C, heated on the water bath, and then taken to dryness, finishing in an air bath at 120°C. The residue is

treated with 20 c.c. of the same hydrochloric acid, heated to boiling, diluted with three times its volume of water, and filtered from silica. The filtrate is evaporated to a small volume until hydrochloric acid begins to escape, 10 c.c. of concentrated hydrochloric acid added, and then oxidised with 2-2.5 c.c. of nitric acid of specific gravity 1.4, added drop by drop to the boiling liquid. The product is then evaporated on the water bath to a syrupy consistency, or until a basic chloride begins to separate. The resulting solution, which should measure about 10 c.c. is transferred to a specially constructed separator, and 55-60 c.c. of hydrochloric acid of the strength mentioned above, added, and the whole shaken out twice with ether. Should copper or cobalt be present, its removal must be provided for in the manner already described. When the separation of iron and aluminium is effected by this process, particular care must be taken that the solution in the separator is quite clear and free from any basic salts of the latter metal. The author gives analytical figures showing the reliability of the process, and states that it has been used in more than 100 analyses of iron, steel, and ferromanganese, with successful results.

B. B.

**New Colour Standard for Natural Waters.** A. Hazen. (*Amer. Chem. J.* xiv. 300-310.)

Leeds suggested the adoption of nesslerised ammonia as a standard for comparison with the colour of natural waters, degrees of colouration being expressed by the number of c.c. of dilute ammonia solution (0.01 mgm.  $\text{NH}_3$  per c.c.) which, when nesslerised in 50 c.c. of distilled water, match the colour of the natural water. An insurmountable objection to the method is the variable character of the colour obtained by nesslerising ammonia; both temperature and quality of nessler reagent influence the colouration.

Crookes, Odling and Tidy use an empty tube of the same length as that containing the water to be compared; this has two hollow wedges behind it, the one filled with a 1 per cent. copper sulphate solution and the other with a mixture of ferric chloride (0.7 gram. per litre) and cobalt chloride (0.3 gram. per litre) solutions with "a very slight excess of hydrochloric acid." These wedges are pushed over the empty tube until the colour, on looking down it, appears identical with that of the water. In this case degree of colouration is expressed as equivalent to so many mm. of blue, and so many mm. of brown solution. The colours of these solutions are, however, variable both with temperature and quantity of hydrochloric acid present.

The author proposes a platinum colour standard, the colour to be expressed as "the amount of platinum, in parts per 10,000, which, in acid solution, with so much cobalt as will match the hue, produces an equal colour in distilled water." The standards are made thus:—1.246 grms. of potassium platinic chloride (0.5 gram. Pt.) and 1 gram. of crystallised cobalt chloride (0.25 gram. Co.) are dissolved in water, 100 c.c. of strong hydrochloric acid are added, and the whole is made up to 1000 c.c. This stock solution will



remain unchanged for a long time, even when exposed to light. For comparison with waters, 1, 2, 3, etc., c.c. of the stock solution are diluted to 50 c.c. in Nessler tubes. These correspond to 0.1, 0.2, 0.3, etc., degrees of colour standard. These also keep for months, in absence of dust. If the hue do not match that of the water, more or less cobalt may be added, the platinum being kept constant.

Direct comparison in 200 mm. Nessler tubes is generally sufficiently accurate. But when the colour is of great importance, the author uses 600 mm. brass tubes (washed internally with lead acetate solution, to destroy reflection) with plate-glass ends; and instead of mixing the stock solution with the distilled water he places behind the tube containing the latter, flat jars of solution corresponding to 0.01, 0.02, 0.03, etc., degrees of colour. The solution in the jars must be as many times stronger than that which would have been used had the tube been filled with it, as the tube is longer than the thickness of the jar.

For waters more than very slightly turbid and of more than 0.3 degrees of colour, the 600 mm. tubes are not good. For those of more than 0.9° the 200 mm. tubes are not good. Between this and 1.8° 100 m.m. tubes may be used.

Some remarks on the variation of the absolute colour produced by Nessler's reagent with the same quantity of ammonia under varying conditions,--which, however, do not occur in the usual determination of ammonia,—and a comparison of the Nessler standard with the platinum standard for the colour of a water, conclude the paper.

A. G. B.

**Estimation of Sulphur in Pyrites Cinders.** G. Lunge. (*Zeits. angew. Chem.*, 1892, 447; through *Chem. Zeit.*)—The author conducts Watson's method as follows:—3.2 grams of cinders are mixed with 2 grams of sodium bicarbonate of known titre, and heated in a nickel crucible (20 grams capacity) for 10—15 minutes, so that the point of the flame shall only play upon the bottom of the crucible, the bicarbonate being thus decomposed. The heating is continued for 15 minutes over a stronger flame, so that the whole mass becomes red hot. Fusion is to be avoided, and the crucible must be kept covered. The cooled mass is turned into a porcelain dish; if the temperature has been high enough it will be black and porous, otherwise it will be glassy and difficult to dissolve. After digestion with hot water, a strong solution of sodium chloride, carefully made neutral to methyl orange by hydrochloric acid, is added to the solution in order to obtain a clear filtrate; for the same purpose the filter paper should be first washed with the salt solution. The liquid having been decanted on to the filter, and returned if it come through of a yellowish green colour, the residue is digested with more of the salt solution, and finally washed with a dilute salt solution. The filtrate and washings are titrated with pentanormal hydrochloric acid. The sulphur is calculated from the amount of bicarbonate which has been converted into sulphate, as determined by the decrease in alkalinity.

A. G. B.

**Estimation of Acetone.** **H. Strache.** (*Wien Monatshefte für Chemie* 1892, xiii., 299-315.)—The chemistry of this process may be summed up in the statement that the hydrazones, which phenylhydrazine forms with aldehydes and ketones, are incapable of oxidation, with liberation of nitrogen, by Fehling's solution, whereas phenylhydrazine itself is quantitatively so oxidised at the boiling point of the solution, with liberation of all its nitrogen. The readiest method, therefore, for determining the amount of hydrazone produced by the reaction between an aldehyde or a ketone, and excess of phenylhydrazine, is to boil the mixture with Fehling's solution and measure the evolved nitrogen.

A weighed quantity (probable excess) of phenylhydrazine hydrochloride is dissolved in warm water together with  $1\frac{1}{2}$  times its weight of sodium acetate. A measured quantity of the liquid containing the acetone is added to the solution, and the whole is heated on the water-bath for 15 minutes. The volume is now made up to 100 c.c., and 50 c.c. are transferred to the separating funnel of the apparatus described in the following paragraph, the stem of the funnel having been previously filled with water.

A convenient quantity (200 c.c.) of Fehling's solution is placed in a flask ( $\frac{3}{4}$ —1 litre) which is provided with a three-holed cork. One of the holes carries a tube which passes to the bottom of the flask and is connected with another flask for supplying steam. The second hole is for the separating funnel; the end of this reaches to the bottom of the flask and is drawn out and curved upwards to prevent gas from escaping up the stem. Through the third hole passes the tube which is to deliver the nitrogen into the measuring tube.

The Fehling's solution is heated to the boiling point and a rapid current of steam is passed through the apparatus, until the air has been expelled as completely as possible. The phenylhydrazine mixture is then allowed to flow from the funnel into the flask very slowly at first, in order to avoid cooling the liquid in the flask and creating a back-suck. The nitrogen is very rapidly evolved and swept on by the current of steam, the whole operation only occupying two or three minutes. Inasmuch as benzene is a product of this reaction, the nitrogen will contain the vapour of that compound; allowance must be made for this in measuring the gas, which is best saturated with the vapour by allowing a few drops of benzene to rise up the water in the measuring tube. The following are the corrections to be made for the tension of benzene + water at various temperatures:—

|        |          |        |          |
|--------|----------|--------|----------|
| At 15° | 72.7 mm. | At 21° | 98.8 mm. |
| „ 16°  | 76.8 „   | „ 22°  | 103.9 „  |
| „ 17°  | 80.9 „   | „ 23°  | 109.1 „  |
| „ 18°  | 85.2 „   | „ 24°  | 114.3 „  |
| „ 19°  | 89.3 „   | „ 25°  | 119.7 „  |
| „ 20°  | 93.7 „   |        |          |

The difficulty of completely expelling the air from the flask tends to make the volume of the gas measured too large. Thus, the author found, as a mean of 8 experiments, that 1 gm. of phenylhydrazine hydrochloride gave 159.7 c.c. of nitrogen instead of 154.6 c.c. This error is, however, nearly constant for the same flask and is best avoided by calibrating the apparatus. This can be done by performing a blank experiment with 1 gm. of phenylhydrazine hydrochloride and substituting the volume of gas obtained, for 160 in the following formula, in which  $A$  is the weight of the acetone in grms.,  $g$  the weight of the phenylhydrazine hydrochloride taken,  $V_0$  the corrected volume of the nitrogen evolved, and 0.002595 the acetone equivalent to 1 c.c. of nitrogen:—

$$A = [160g - 2 V_0] 0.002595$$

The acetone from a very dilute solution may be determined by boiling the liquid in a flask provided with a small absorption tube containing the phenylhydrazine solution. A current of air will hasten the distillation of the acetone into the phenylhydrazine.

The author hopes to apply this method to the determination of aldehyde, and possibly of alcohol by first converting it into aldehyde.

A. G. B.

#### A New Method for the Determination of Carbon in Organic Substances.

K. Okada. (*Arch. Hyg.* xiv. 364, through *Chem. Zeit.*)—The author has found that when organic substances are heated with sulphuric acid, as in the Kjeldahl process, only carbon dioxide is formed, no other volatile compounds containing carbon being evolved. This circumstance makes it possible to determine carbon by the method in question, and in the case of substances containing nitrogen, to estimate that element at the same time and by the same operation. The flask in which the operation is conducted, is provided with a glass tube ground-in, connected with a wash bottle, this in its turn is coupled with a second washing flask, and finally with a Pettenkofer's tube. The first wash bottle contains water, and the second permanganate, and the absorption tube is filled with baryta water to receive the carbon dioxide. At the end of the operation the apparatus is connected with a water pump, and air free from carbon dioxide drawn through it. The usual Kjeldahl mixture, of ordinary and fuming sulphuric acid, is used with the addition of a little mercury. The analytical results are concordant, and the process appears applicable to a number of substances. The author is engaged in devising a method of determining oxygen on the same lines.

B. B.

**The Examination of Commercial Yolk of Egg.** M. F. Jean. (*Monit. Scient.* 1892, vi. 561, through *Chem. Zeit.*)—The author has confined his examination of fresh and salted yolk of egg to the determination of the water, the dry extract, the vitellin, the extractives soluble in water and the ash. The water is determined by adding a few drops of acetic acid to 10 grms. of the sample, drying first at 50°–60°C and then at 110°C, until the weight is constant. In order to determine the fat and the vitellin,

the dried residue is extracted with petroleum ether in a Soxhlet apparatus, the ether-extract evaporated to dryness, and the residue dried at 110°–115°C, and extracted with water. This aqueous extract is evaporated on the water bath and afterwards heated to 110°C. The residue thus left consists of water-soluble extractives which are taken as soluble vitellin. The residue insoluble in water is the fat. The ash is determined by incinerating 10 grms. of the sample in a platinum dish (at first at a low temperature), until the residue is white. When the water, fat, ash and water-soluble extractives are known, the difference is put down as insoluble vitellin, and this added to the soluble vitellin already estimated gives the total vitellin. The salts found in the ash are sodium chloride, sulphate, borate, and nitrate. Of these it generally suffices to determine the first, which is best done on the aqueous extract of a fresh quantity of the yolk of egg, dried at 100°C, rather than on the total ash. An average sample of fresh yolk of egg, analysed in the manner given above, contained water 52.6, ash, 1.4, fat 28, and vitellin 18 parts per cent. respectively.

B. B.

**The Rising of Cream in Watered Milks.** Allard. (*Staz. Sper. Ag. Ital.*, xxii., 420, from *La Laiterie*).—The author made comparative experiments as to the time taken by the cream in rising in a sample of undiluted milk, and the same milk diluted with 10, 20, 40, 50, 60 and 75 per cent. of water.

In genuine milk a distinct stratum was observed after 90 minutes (2.5 per cent.), while in that diluted with 50 per cent. of water 45 minutes only was requisite. The total quantity of cream (14.1 per cent.) was thrown up by genuine milk after 27 hours, by that diluted with 10 per cent. of water (13.3 per cent.) in 23 hours, 20 per cent. (12.5 per cent.) in 17 hours, and 40 per cent. or more in 2 or 3 hours.

The author remarks that if a milk throws up its cream in 3 hours the conclusion may be drawn that the pump has passed that way.

H. D. R.

[NOTE BY ABTRACTOR.—Vieth has shown (*ANALYST*, viii., 2), that some samples of genuine milk throw up their cream very rapidly; it is well known that no reliance can be placed on cream-tests on milk that has been refrigerated, and has had much shaking in transit, and this test is thus deprived of its value. As it will only give indications of extensive watering (40 per cent.), the lactometer would be much simpler and more reliable.]

H. D. R.

**Citric Acid.** T. Fusch. (*Pharm. Zeit.*, 1892, xxxvii., 448; through *Chem. Zeit.*)—The author claims that citric acid may be stated to be free from lead when 50 c.c. of a 10 per cent. solution of it, contained in a beaker placed on a white surface, shows no darkening with sulphuretted hydrogen. Citric acid, absolutely free from lead, has been made in Germany for several years.

A. G. B.

**Estimation of Lime Salts in Syrup and Sugar Products.** J. Wolff. (*Oestr. ungar. Zuck. Ind.* xxi. 96—104. through *Chem. Centr.*)—The author effects his object by means of a soap solution. This is prepared from pure olive oil (150 grms.) by saponification with finely-ground litharge (100 grms.) and a solution of lead acetate (5 grms.) in water (40 c.c.) at 100°. The lead soap is washed, and after being softened on the water bath, 150 grms. of it are decomposed by trituration, with 40 grms. of potassium carbonate. The potash soap is extracted with alcohol, and the alcohol distilled off; 40 grammes of the residue are dissolved in a litre of alcohol of 56 Tralles (*sic*). This solution is then brought to such strength that 1 c.c. corresponds to 0.0005 gm. of CaO. The titrations necessary for this are effected thus:—100 c.c. of standard calcium chloride solution (0.15 gm. per litre), 25 c.c. of pure syrup, some drops of strong ammonia and water to make 150 c.c., are put into an Erlenmeyer flask, into which the soap solution is run until the addition of a drop produces a bright vesicular lather, about 1 c.m. thick, and permanent for at least 10 minutes. The operation must be repeated without the presence of calcium chloride, and the difference between the results held to be the number of c.c. equivalent to 100 c.c. of the calcium chloride solution.

The estimation of lime salts in sugars is carried out in the same way, only care must be taken to obtain a genuine lather. To this end the presence of ammonia is desirable, and the quantity of soap solution necessary should not exceed 20 c.c.; the qualifications required of the lather, detailed above, must be insisted upon, and when it has disappeared it should be easily re-formed by another shaking.

A. G. B.

**Effect of "Centrifuging" on Bacteria in Suspension.** (*Arbeit a. d. Kaiser. Gesundheits-Amte*, vii. (1891) through *R. M. S. JI*, 1892 p. 432.)—After having ascertained by experiments with anthrax that an hour's "centrifuging" at the rate of 2,000 to 4,000 turns per minute was not detrimental to the vitality or the virulence of these organisms, Herr Scheurlen turned his attention to the behaviour of bacterial pure cultivations in suspension.

The results of centrifuging were found to differ according as the bacteria were mobile or immobile, the latter being thrown out and forming a sediment, while some of the former, *e.g.*, Cholera Vibrio and Proteus Mirabilis, remained suspended.

The author then examined the behaviour of the bacteria of milk when similarly treated. After centrifuging, the milk serum, when tested by means of plate-cultivations, showed, as was to be expected, a large number of colonies; while the number in the cream was also very great, and might even exceed that of the serum. The author infers from these experiments that milk cannot be freed from its bacteria by centrifuging, for out of 2,050 million germs in the whole volume of milk, only 18 million were removed in the serum. About three-fourths of the number are transferred by the centrifuging to the cream, the remainder being in the butter-milk.

Most pathogenic microbes, such as anthrax, typhoid, and cholera, cling to the cream like the milk bacteria, but tubercle bacilli were for the most part separated out, only a few remaining in the milk and cream.

F. H. P. O.

## REVIEW.

COMMERCIAL ORGANIC ANALYSIS. By ALFRED H. ALLEN. Second Edition, Volume III., Part II. (London, J. and A. Churchill, 18s.)

We welcome the appearance of this further instalment of the Second Edition of Mr. Allen's great work. The matter has grown under Mr. Allen's hands to such an extent that Vol. III. will, when completed, consist of three separate volumes, of which the one under review comprises 570 pages, and treats of the Amines, Hydrazines, Tar Bases, and Vegetable Alkaloids, the last section occupying almost four-fifths of the volume. The chapters on the characters, reactions, and isolation of alkaloids convey in a most lucid manner an immense amount of practical information. The colour-reactions, in particular, are treated in an admirable manner, and more sound analytical information is given by the author in the pages devoted to this subject than in any work on toxicology with which we are acquainted. Mr. Allen enumerates in a concise way the various alkaloids which with dehydrating, oxidising, and other reagents give characteristic colours, and thus enables the analyst almost at a glance to identify an alkaloid under examination. The special chapters on aconite, opium, and cinchona alkaloids bear witness to Mr. Allen's thoroughness, and present exhaustive reviews of the most recent researches on these difficult and intricate subjects. The practical aspects are always kept fully in view, and the analyst will find all he may require in reference to morphimetry, the assay of barks, and the separation of cinchona bases. Of special interest to the public analyst is Mr. Allen's treatment of caffeine and its allies, under which head the composition and analysis of tea, coffee, and cocoa are considered in detail, and in a manner vastly more accurate and scientific than has been the case in any manual specially devoted to food analysis. The author's special knowledge of these subjects renders these chapters of the greatest value. Modern processes of precision will here be found recorded, and in many cases critically discussed. Mr. Allen's work appears to us the type of what a chemical treatise ought to be. Science and practice are blended on every page. We are fully familiar with purely chemical works to which the analyst often turns, and vainly so, for help and information when he has to solve a problem new to him, only to find that they too often avoid giving useful data to the practical worker. We are equally familiar with the practical works on analysis, especially of food, which are too often devoid of good, sound science. In Mr. Allen's volume, modern science and accurate description of the properties, chemical and physical, of the substances with which he has to deal are combined with concise descriptions of analytical processes, and with such information to the analyst that the work will be found a real and trustworthy laboratory friend. It is rare indeed that an author combines the scientific with the practical side as does the author of "Commercial Organic Analysis." The earlier edition of this work has been recognised to be of the utmost value to the practical chemist, and this second edition, which is in reality a new work, will be found indispensable to every analyst who desires to keep up with the rapid progress of organic analysis. We look forward with interest, and something like impatience, to the one volume now remaining to be issued.

O. H.







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